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THE LOS ANGELES CATALYST STUDY SYMPOSIUM

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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The proceedings consist of 21 technical papers covering such areas as sampling and analytical methods for aerosols, including NH$_4^+$, SO$_4^=$, Pb and NO$_3$; quality assurance procedures; statistical analysis of LACS data; and trends in ambient air pollution concentration measured just off a heavily travelled roadway in Los Angeles.

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FOR DISCUSSION OF
THE LOS ANGELES CATALYST STUDY

Proceedings

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April 12 and 13, 1977

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FOREWORD

Careful assessment of the relative risk of new man-made environmental hazards is necessary for the establishment of sound regulatory policies. In 1974, the Environmental Protection Agency (EPA) established an interdisciplinary research program to determine the environmental risk of emissions from vehicles equipped with oxidation catalytic control devices. One major area of emphasis in this program has been the operation of a long term roadside monitoring study to quantify ambient levels of catalyst vehicle emission products.

The Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina, has conducted the Los Angeles Catalyst Study since June, 1974, before the introduction of the 1975 model year catalyst equipped automobiles. Through a combination of careful site selection and study design, best-technology sampling equipment, experienced personnel, and a carefully created quality assurance program, an extensive and reliable data base has been generated for a multitude of ambient pollutants relating to automotive emissions. The Los Angeles Catalyst Study site has also proved to be an excellent location for evaluating the performance parameters of the newer methods applied to the measurement of catalyst emission products.

Information presented in this Symposium Proceedings document highlights the various aspects of the Study operations. The critical area of trend assessment is addressed along with a detailed discussion of quality assurance measures used to establish the reliability of trend data. Overall, the Los Angeles Catalyst Study is providing a sound data base upon which EPA can make a responsible appraisal of the impact of the catalyst control technology on the ambient environment.

Thomas R. Hauser
Acting Director
Environmental Monitoring and Support
Laboratory
Research Triangle Park, North Carolina

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INTRODUCTION

A symposium was held on April 12 and 13, 1977 at Raleigh, North Carolina for discussion of the Los Angeles Catalyst Study. Welcoming remarks were presented by Dr. Thomas R. Hauser, Acting Director of the Environmental Monitoring and Support Laboratory, EPA, Research Triangle Park, North Carolina. Dr. Hauser, who chaired the Symposium, introduced the first speaker, Albert C. Trakowski, Deputy Assistant Administrator, Office of Monitoring and Technical Support. Mr. Trakowski informally profiled the background details of the Study. His comments and the formal papers which formed the basis of the meetings are presented here in order of occurrence.

ORIGINS OF THE LOS ANGELES CATALYST STUDY

A. C. Trakowski

Environmental Protection Agency
Washington, D. C.

It seems almost customary that meetings held where the knowledge is - are opened with kind words by someone from that place where the knowledge "ain't". On this occasion I'm very pleased to be that person, to have the opportunity to meet you and at least in part participate in the review of this project that had its origin just about four years ago. Other than tell you how nice it is to be here to see what can be told from the data that has been in collection for nearly three years, it might serve us all well to go over the events that led into this project. It was, you know, set up for some clear purposes. And those purposes, in turn, had their causative stimulations.

I'm not quite sure who or where it was that concern was first expressed about sulfate emissions from automotive catalyst converters. It dates back to mid or late 1972. But, in the early months of 1973 it was generally recognized, at least in the technological community, that sulfuric acid emissions from catalyst equipped cars could possibly cause a harmful effect on both the environment and on the health of people. In November 1973, the Administrator of EPA, Russell Train, presented his views to the U.S. Senate Public Works Committee concerning the introduction of catalytic converters on 1975 model year cars. Testimony was also presented at that Committee hearing by various automobile manufacturers, the petroleum industry, environmentalists, various consultants and other special interest groups. During his testimony to the Committee, Mr. Train summarized the events leading up to his decision to make no changes in the previously promulgated emissions standards for 1975 model year cars and to take no action that would inhibit the use of catalysts on 1975 cars. His testimony included his recognition of possible risks from the use of catalytic converters, but he expressed the belief that the use of catalysts on cars held much promise for the reduction of atmospheric pollution.

He explained to the Senate Committee how a catalyst functions to reduce the levels of hydrocarbon and carbon monoxide emissions. Mr. Train went on to tell how the sulfur in the fuel is converted to sulfate by the catalyst and that the amount of sulfate emitted from the cars to the atmosphere could possibly be at a level that would present a new and different danger to the health of exposed people. He discussed how EPA had projected the quantity of possible sulfate emissions from catalyst equipped cars and its anticipated effect on air quality. However, his bottom line was an acknowledgement of the limitations of EPA's knowledge on the entire subject of the effect on the environment of sulfate, platinum, and other emissions from catalyst equipped cars.

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In making his decision to allow the go-ahead for use of catalysts, Mr. Train was forced to consider several very difficult issues which demonstrated the complexities that had to be faced in EPA's efforts to improve the quality of the air environment and protect the nation's health. Some of these issues were:

First, a comparison of the effects on public health with or without catalysts on automobiles;

Second, methods to insure protection from sulfate emissions if further studies indicated such actions were necessary;

Third, effects of the catalyst on the momentum of the nation's total air pollution control effort;

Fourth, impact on energy conservation; and

Last, effects on the complete range of technological options available to control automotive emissions, including catalysts.

Addressing these issues before the Senate Committee in November 1973, Mr. Train concluded that if EPA postponed the requirements to control automotive emissions for a year, the nation's overall momentum in achieving health-related air quality standards would suffer. A postponement would have required that some transporation control plans would have had to have been made more stringent.

Also, Mr. Train observed that EPA prohibition would very likely have made the industry dependent on other technologies, some of which were promising, but none of which were ready for mass production. The further we advance new technology, the more we become aware of possible unintended side effects. It was recognized that as other technologies came closer to massive application, that they may likewise exhibit undesirable side effects.

Additionally, there was the point that the use of catalysts enabled the use of more efficient automobile engines, which offered potential for reducing gasoline consumption, thereby having a favorable effect on energy conservation.

Of course, his decision was based on the need for comprehensive protection of public health. Mr. Train stated that in the time then to come, EPA would be able to learn much more about how to measure sulfate emissions from cars, their impact on public health, and how to control these emissions.

So--it was at that time, in November 1973, that Mr. Train made the decision to take no action that would prevent the use of catalysts on 1975 cars. But he simultaneously announced that EPA would carry out several tasks to develop the information necessary to make future judgments concerning the effects of his decision. These intended tasks were:

First, EPA would accelerate work on developing a test procedure of assured reliability for measuring emissions of sulfates from cars;

Second, EPA would consider all feasible measures for controlling sulfate emissions from cars, including a regulatory approach for controlling sulfur content in gasoline, and other alternatives. In addition, EPA would encourage the petroleum industry to voluntarily make available unleaded gasoline of low sulfur content for the 1975 model vehicles;

Third, EPA would improve its ability to estimate the impact of sulfate and other emissions from cars on air quality and public health; and

Last, EPA would improve its understanding of the atmospheric chemistry involved and establish an appropriate air monitoring program, to determine the effects of catalyst equipped vehicles.

To carry out the monitoring program promised by this fourth task, a number of options were analyzed on where to locate it, and a decision was made in March 1974 to carry out the work in California. Subsequently, the Los Angeles Catalyst Study was initiated in June 1974. The prime objectives of this study were fourfold:

- *To determine the impact of catalyst equipped cars on air quality for automobile related pollutants.*
- *To establish the ambient levels of carbon monoxide, lead, and sulfur dioxide in order to determine the surrogate sulfuric acid ambient levels.*
- *To provide an active data base to compare the effects of pre- and post-catalyst automobiles.*
- *To evaluate and improve field methods for detection and measurement of air quality changes relatable to catalyst emissions.*

Now we are here, nearly three years later, to see how we've done and what we've discovered. Has the use of the catalytic converter affected the ambient level of automobile pollutants - especially along-side heavily travelled roads? As they said in the old days - "stay tuned to find out."

But before revealing the solution to our mystery. let's go into how the sleuthing was planned and carried out. Our next speaker, Mr. Franz Burmann will discuss the LACS study design, pre-study considerations, and essentially take up where I leave off.

Thank you very much. You have my very best wishes for a most successful symposium.

LOS ANGELES CATALYST STUDY DESIGN

Franz J. Burmann

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The Los Angeles Catalyst Study came into being because of public concern over the possible adverse impact of emissions from catalyst-equipped automobiles on the ambient air. The study was to be a comprehensive long-term investigation of the ambient levels of sulfuric acid aerosol, sulfates, and other potential catalyst emission products in areas adjacent to a heavily traveled freeway in Los Angeles. Based on this general objective, the Environmental Monitoring and Support Laboratory proceeded to design a roadside study to monitor pollutant levels on both sides of a freeway for a projected 3-year period. In order to obtain data prior to the introduction of catalyst-equipped vehicles the study had to be designed and initiated in a very short time. After delineating specific study objectives, the selections of the pollutants and related measurements to be monitored were made. The required quality control measures were determined and consideration given to the need to maintain the desired level of data precision and interlaboratory comparability. In that the ambient level measurement technology for sulfuric acid was not available, a variety of sulfur compounds and related auto-emission products were selected to provide the basic on which to estimate sulfuric acid concentrations. In order to minimize interfering effects from extraneous pollutants, high background levels, and unfavorable meteorology, an intensive effort was made to select a site in Los Angeles that met a prescribed list of siting requirements. The site selected on the San Diego Freeway in West Los Angeles provided predominant cross-freeway wind flow, such that identical upwind and downwind measurements could be made to assess the contribution from the freeway. A short-term study was subsequently performed which verified that during favorable meteorology periods the upwind "background" site did provide measurements unbiased by the freeway emissions. Overall the study design has been shown to be excellent for the assessment of the original objectives.

STUDY DESIGN

To explain the Los Angeles Catalyst Study (LACS) design, it is desirable to review briefly some of the estimates of increases (incremental) sulfate ($SO_4^=$) exposure which were expected to result from the introduction of the catalyst. The Environmental Protection Agency (EPA) estimated human exposures from locally increased concentrations by considering ambient air quality and

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human activity patterns (Table I). The three independent techniques used to estimate exposure were:

- *Use of dispersion models developed for emissions of carbon monoxide (CO),*
- *Use of lead (Pb) surrogate data, i.e., the Pb/SO_4 ratio of emission rates to project ambient $SO_4^=$ levels,*
- *Use of the carboxyhemoglobin surrogate method. This method avoids assumptions about traffic or human activity patterns but depends, among other assumptions, on an assumed relationship between CO and suspended particulate $SO_4^=$ emission rates.*

Table I shows the estimates for short term incremental exposures to suspected particulate sulfates and sulfuric acid emitted from vehicles equipped with oxidation catalysts obtained by the CO dispersion model and the Pb surrogate for various receptors under selected meteorological conditions. Concentration estimates are shown for four different receptor locations. The concentration on automobile passenger or driver experience is considered to be similar to that existing at a location in an outer lane. The receptor labeled "Pedestrian Near Expressway" is at a location 3 meters away from the outermost downwind lane. The third receptor, "Nearby Homes" is assumed to be at a location 50 meters from the nearest downwind lane and the receptor labeled "Homes about 5 blocks from Expressway: is assumed to be 500 meters downwind of the highway.

Estimates were made for two types of meteorological conditions. The "Normal Meteorology" can be characterized by light to moderate wind speed of 4 meters per second and a slightly unstable atmosphere. The "Worse" Meteorology" consists of a barely perceptable drift of the wind at 0.5 meters per second and a slightly stable atmosphere. Two wind directions were considered for the estimates: (a) wind directly across the highway and (b) a wind direction at an angle which resulted in the highest calculated concentration for a given receptor. Based on the dispersion model used, the worst angle varies from nearly parallel to the highway for near receptors, to larger angles for more distant receptors.

In addition to those listed in the table, two further assumptions are made in applying the CO dispersion model: (a) acid aerosols and fine particulate sulfates disperse as does CO, and (b) a one-hour commuter trip of 30 miles on a ten lane expressway with traffic flow of 20,000 vehicles per hour is typical. The Pb surrogate estimates might be affected by the settling of Pb particles near the roadside which would tend to underestimate the predicted sulfate concentration. Conversely, if re-entrainment of settled Pb particles occurs, overestimation of incremental sulfate is possible. However, as can be seen in Table I the projected sulfate concentrations by the method are in the general range of values predicted by the CO dispersion model. Data from the carboxyhemoglobin surrogate method (not shown) were also in this general range.

TABLE I. PREDICTED SHORT-TERM INCREMENTAL EXPOSURES TO SUSPENDED PARTICULATE SULFATES AND SULFURIC ACID EMITTED FROM VEHICLES EQUIPPED WITH OXIDATION CATALYSTS*

Human Exposure	Highway Source	Method of Estimation	Incremental Exposure (micrograms per cubic meter)			
			Normal Meteorology		Worst Meteorology	
			Wind Directly Across Highway	Wind at Worst Angle	Wind Directly Across Highway	Wind at Worst Angle
Automobile Passengers	Expressway	Dispersion Model	2			
		Lead Surrogate***	4 to 5	7	22	124
Pedestrians	Near Expressway	Dispersion Model	2			
		Lead Surrogate***	3 to 7	5	20	88
Pedestrians	Urban Street** Canyon	Dispersion Model	4 to 6			
		Lead Surrogate***	2 to 9	-	--	--
Nearby Homes	Expressway	Dispersion Model	1	2	19	33
Homes About 5 Blocks Away	Expressway	Dispersion Model	0.3	0.3	5	6

*Emission assumptions: 25% of vehicle miles traveled on busiest multilane expressway (20,000 vehicles per hour at 30 mph by vehicles) equipped with oxidizing catalysts emitting .05 grams of sulfuric acid or sulfate per vehicle mile: Ohter 75% of vehicle miles involve no emissions of sulfuric acid and suspended sulfate. Peak hourly values are tabled.

**Assumes 10,000 vehicles per hour instead of 20,000. Actual observed carbon monoxide values in medium sized suburban shopping center indicate that peak hourly exposures to 4.5 to 5.3 μg/m^3 of carbon monoxide and by inference 1 to 2 μg/suspended sulfates and acid aerosols would occur.

***Computed by multiplying observed lead levels by adjustments for differences in emissions per vehicle mile and percentage of vehicle miles emitting the particulate of interest: (observed lead level) X (.25) or .18 times observed.

For pedestrians near expressways the incremental exposure estimates ranged from 2 to 88 micrograms per cubic meter ($\mu g/m^3$) of particulate sulfates and sulfuric acid depending on the meteorology. The same calculation indicated 20 $\mu g/m^3$ for the worst meteorological conditions and the wind directly across the highway. Even with normal meteorology the estimates ranged from 2 to 7 $\mu g/m^3$. These predictions were, because of the feared health consequences, of great concern to EPA. With these projections as a background, the Environment Monitoring Brach (EMB) of the Environmental Monitoring and Support Laboratory (EMSL) initiated the design of the LACS.

OBJECTIVES

The primary objective of the study is to determine the impact of catalyst equipped cars on ambient air quality. To achieve this goal it was decided to attempt to obtain a data base for freeway contribution of emission products by monitoring the ambient air adjacent to a heavily travelled highway before and after the 1975 model year catalyst equipped automobiles were introduced. In addition the study's objectives are:

- *to determine the ambient levels of CO, Pb, and sulfur dioxide (SO_2) in order to determine the surrogate (predicted) sulfuric acid (H_2SO_4) ambient levels since technology for measuring ambient H_2SO_4 concentrations was not available, and*

- *to evaluate an improved field methodology for detection of air quality changes attributable to catalyst emissions.*

Since the 1974 model year catalyst-equipped automobiles appeared in California in September or October 1974, it was important that the background sulfate study be initiated as soon as possible to obtain the background data base. Initially, it was estimated that after the appearance of these cars, at least 3 years of monitoring would be required in order to quantify the possible increase in sulfate attributable to catalytic converters.

SITE SELECTION

The California area in and around Los Angeles was the primary area for consideration for several reasons. Because of the more stringent California standards a greater number of vehicles were to be equipped with catalytic converters than in the rest of the nation. The average sulfur content in California gasoline was approximately twice as high as compared to the national average. Traffic density on some of the freeways in Los Angeles approached 200,000 cars/day. The generally low background SO_2 levels in Southern California reduced the possibility of formation of high sulfate background levels.

With only 3 months to set up a full scale field study, the obstacles encountered were formidable. No specific sulfur aerosol samplers were available. Suitable sites were not known nor had been selected, and no sulfate data related to the Los Angeles area had been compiled. A planning meeting was held in late February 1974 with several pertinent groups including EPA's Regional Office (RO) in San Francisco, the California Air

Resources Board (CARB), the Los Angeles Air Polution Control District (LAAPCD), the California Department of Transporation, and the California State Air Industrial Hygiene Laboratory (AIHL). Early in March 1974 extensive discussions were held at the National Environmental Research Center at Research Triangle Park, North Carolina (NERC/RTP), to determine if the site requirements of the Environmental Monitoring and Support Laboratory (EMSL), the Physics and Chemistry Laboratory (PCL), and the Meteorology Laboratory (ML) could be combined. However, it was determined that the 16 stations that were desired by the ML could not be accommodated at the locations under consideration. These particular locations were sought by the ML in order to validate the CO model which had been used as a surrogate to predict sulfate/sulfuric acid levels. A site near Camp Pendleton, located on Highway 5, which could accommodate all of the sites was deemed unacceptable for determination of incremental sulfate increases early enough because of the low vehicle count (fewer than 50,000 vehicles/day). The general consensus was that both needs -- early detection of catalytic attrition products and validation of the CO diffusion model in correlation with any sulfate increases -- were not compatible.

At the end of March 1974 a site selection trip was conducted with the assistance of Rockwell International, under contract to the Environmental Protection Agency (EPA), and consultants of CARB. Criteria considered in relation to an acceptable site were:

- *Predominant perpendicular winds*
- *Probability of low oxides of sulfur (SO_x) contribution from stationary sources*
- *Traffic count approaching 200,000 cars/day*
- *Adequate area for site installation*
- *A freeway elevation near grade*
- *Adequate electrical power availability*
- *Simple lease arrangement and accessibility*

Initially the so-called 42 mile loop (Figure 1) of Los Angeles was investigate. This loop is formed by the San Diego Freeway, the Harbor Freeway, and the Santa Monica Freeway. The loop was of interest since it has traffic count sensors embedded in its freeway ever 3.2 kilometers. On-ramp and off-ramp traffic counts are also recorded and the loop is equipped with traffic control devices. This loop was travelled and carefully searched; however, suitable sites were not found. It was felt that anything south of the vicinity of Manchester Avenue would not be suitable because of the influence of the airport and the many point sources such as refineries. A major refinery, located just south of the airport, is probably one of the worst sulfur point sources in the whole Southern California area.

On the San Diego Freeway south of the Harbor Freeway junction there was a suitable site which was sufficiently open to accommodate the stations,

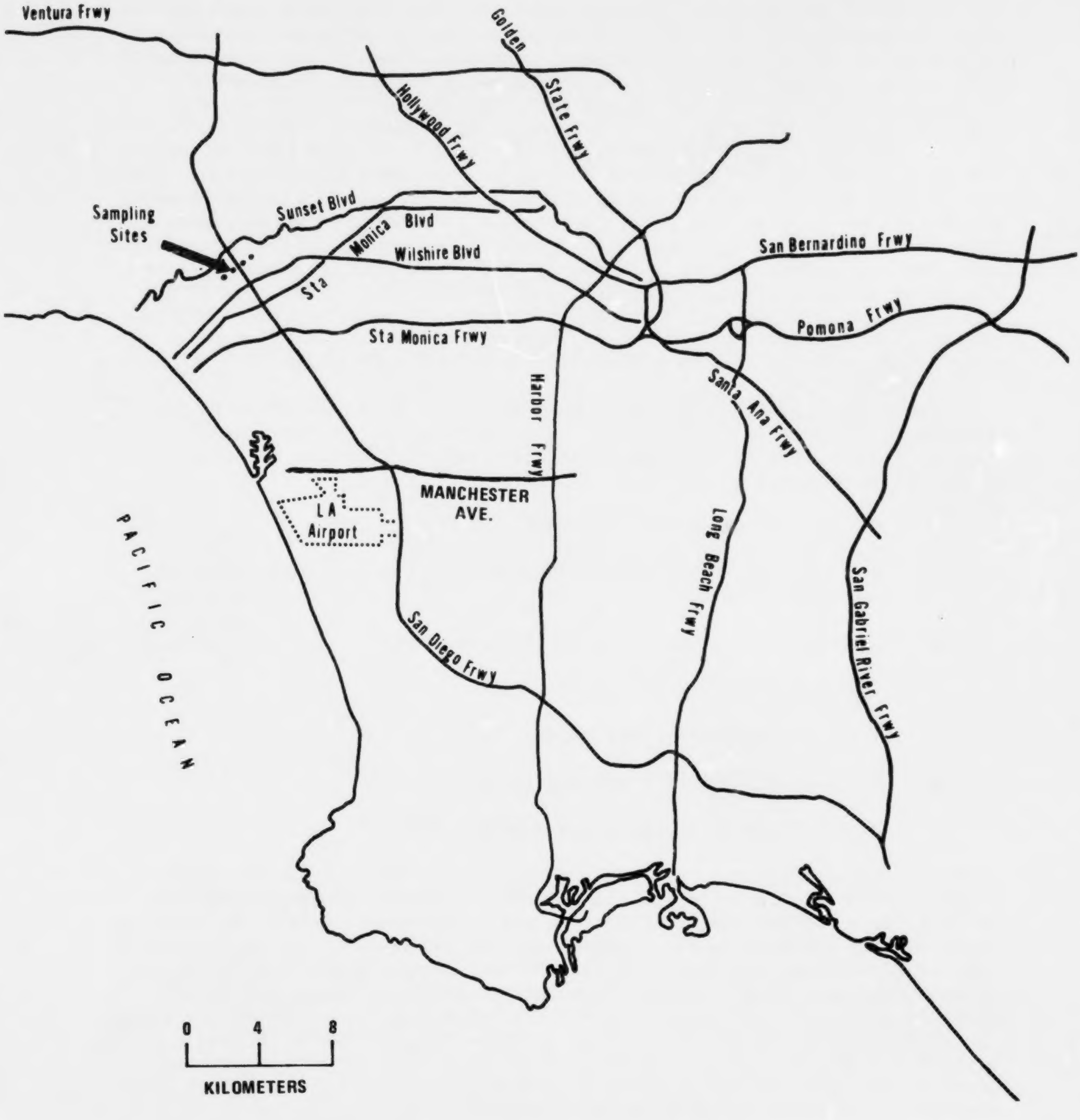

Ventura Frwy
Golden State Frwy
Hollywood Frwy
Sampling Sites
Sunset Blvd
Sta Monica Blvd
Wilshire Blvd
San Bernardino Frwy
Pomona Frwy
Sta Monica Frwy
Harbor Frwy
Santa Ana Frwy
MANCHESTER AVE.
LA Airport
PACIFIC OCEAN
Long Beach Frwy
San Gabriel River Frwy
San Diego Frwy
0
4
8
KILOMETERS

Figure 1. Freeway system of Los Angeles area.

but it was rejected because of the high background levels from the many industrial point sources in the area. Also investigated was the area east of the Santa Ana Freeway and the 605 Freeway (San Gabriel River Freeway), and sites were observed which were sufficiently open. However, the wind field was not very well defined in this area and because of the high smog levels in the summer months, the sulfate background was expected to be too high to determine increases due to the catalytic converters.

After aerial surveillance three potential site locations were indentified The first two sites were located on the Ventura Freeway west of 405. Both of these sites posed problems concerning accessibility and lack of available power. The third potential site was located on the San Diego Freeway near the Wilshire Boulevard off-ramp (Figure 2). On the west side of the San Diego Freeway are the grounds of the Veterans Administration (VA) Hospital and on the east side is the Veterans Cemetry. The sites on both sides of the freeway are about 2 meters below freeway grade. The west side is an open field with power readily available. On the east side, within the fence marking the freeway right of way, a trailer location was available. About 40 meters from the freeway edge due east is the VA cemetery. Wilshire Boulevard, which runs east-west, is about one-half mile south of the location. After consideration of various other possibilities, this last site was chosen for the study.

A graphical overhead view, Figure 3, shows the location of the four platforms that were installed for placement of sampling equipment. Sites A and B were designated "upwind" sites. The two "downwind" sites are labeled C and D. These designations, of course, are only correct for the periods when favorable meteorological conditions exist, i.e., when a seabreeze is prevailing. However, the stations are indeed upwindand downwind very consistently during the daytime hours in the summer months. Therefore, we were able to obtain data on freeway contributions by subtracting background measurements from those made at the downwind site. Although these characterizations do not apply for 24-hour integrated sampling, the designation has been kept to maintain consistency. Data collected at Sites B and D provided an estimate of spatial distribution and yielded some information of freeway contribution during periods of prevailing landbreeze conditions. Figure 4 shows a graphic cross sectional view of the approximately symmetrical placement of the four stations The distance from the edge of the freeway of Sites A and D is approximately 30 meters. The ambient air intake of the samplers is about 1 meter above the freeway surface.

METHODOLOGY

Because CO, Pb, SO_2, and sulfates were the primary pollutants of interest, and methodology was readily available, it was decided to initially monitor these pollutants. The samplers in Figure 4 shown above the dotted lines were on site at the beginning of the study. The principal means of collection for sulfates and Pb were the standard high-volume (hi-vol) sampler and the 102 mm membrane sampler. For CO, nondispersive infrared analyzers were used. For SO_2, the collection procedure of the federal reference method was used. Hi-vol and membrane samplers were programmed to operate initially from 6 to 10 a.m. in the morning, from 3 to 7 p.m., and/or a continuous 24-hour cycle. The morning and evening 4-hour intervals were selected because of the assumed

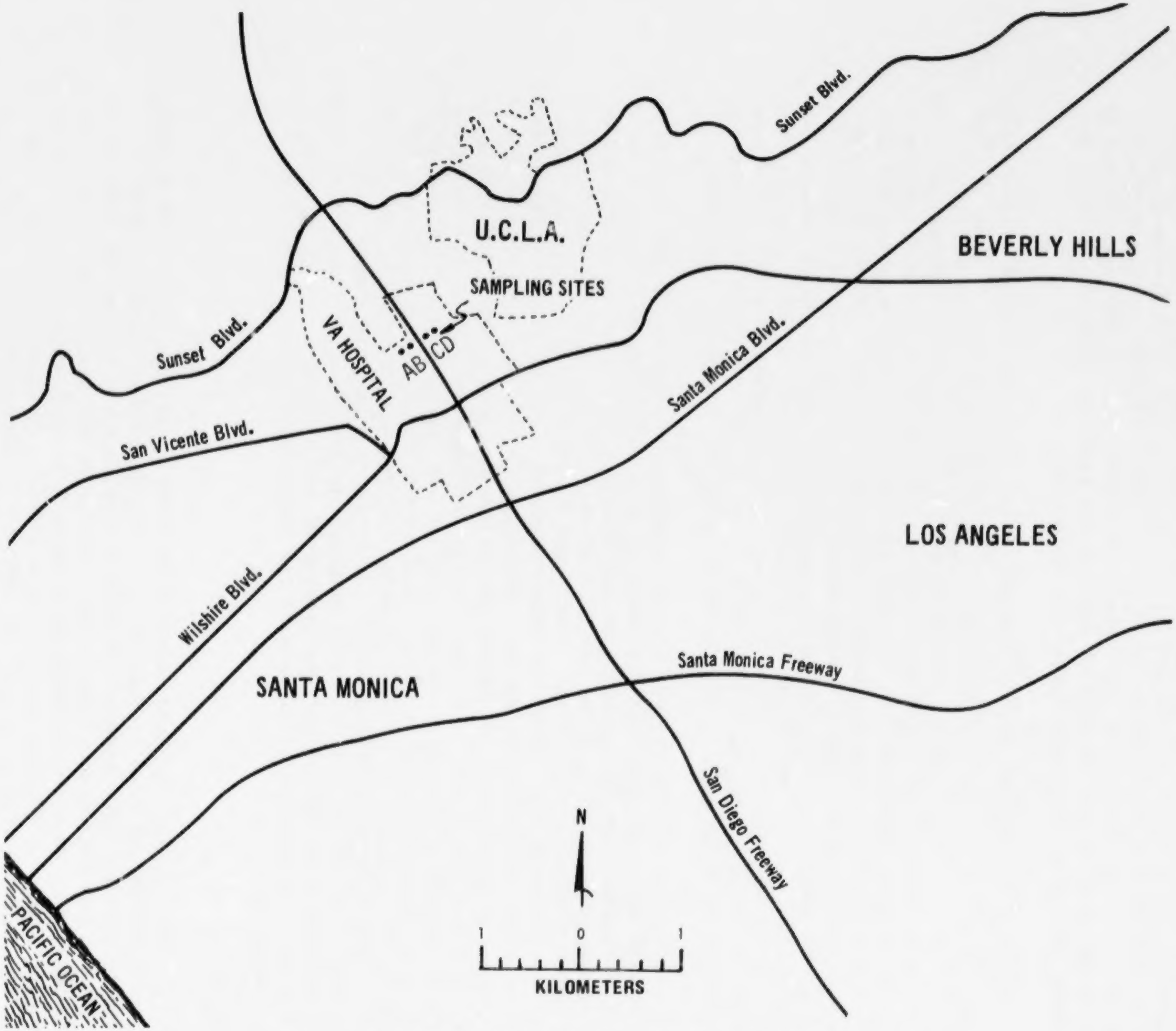

Sunset Blvd.
U.C.L.A.
BEVERLY HILLS
SAMPLING SITES
Sunset Blvd.
VA HOSPITAL
AB
CD
Santa Monica Blvd.
San Vicente Blvd.
LOS ANGELES
Wilshire Blvd.
Santa Monica Freeway
SANTA MONICA
San Diego Freeway
N
1
0
1
KILOMETERS
PACIFIC OCEAN

Figure 2. LACS site location in Los Angeles.

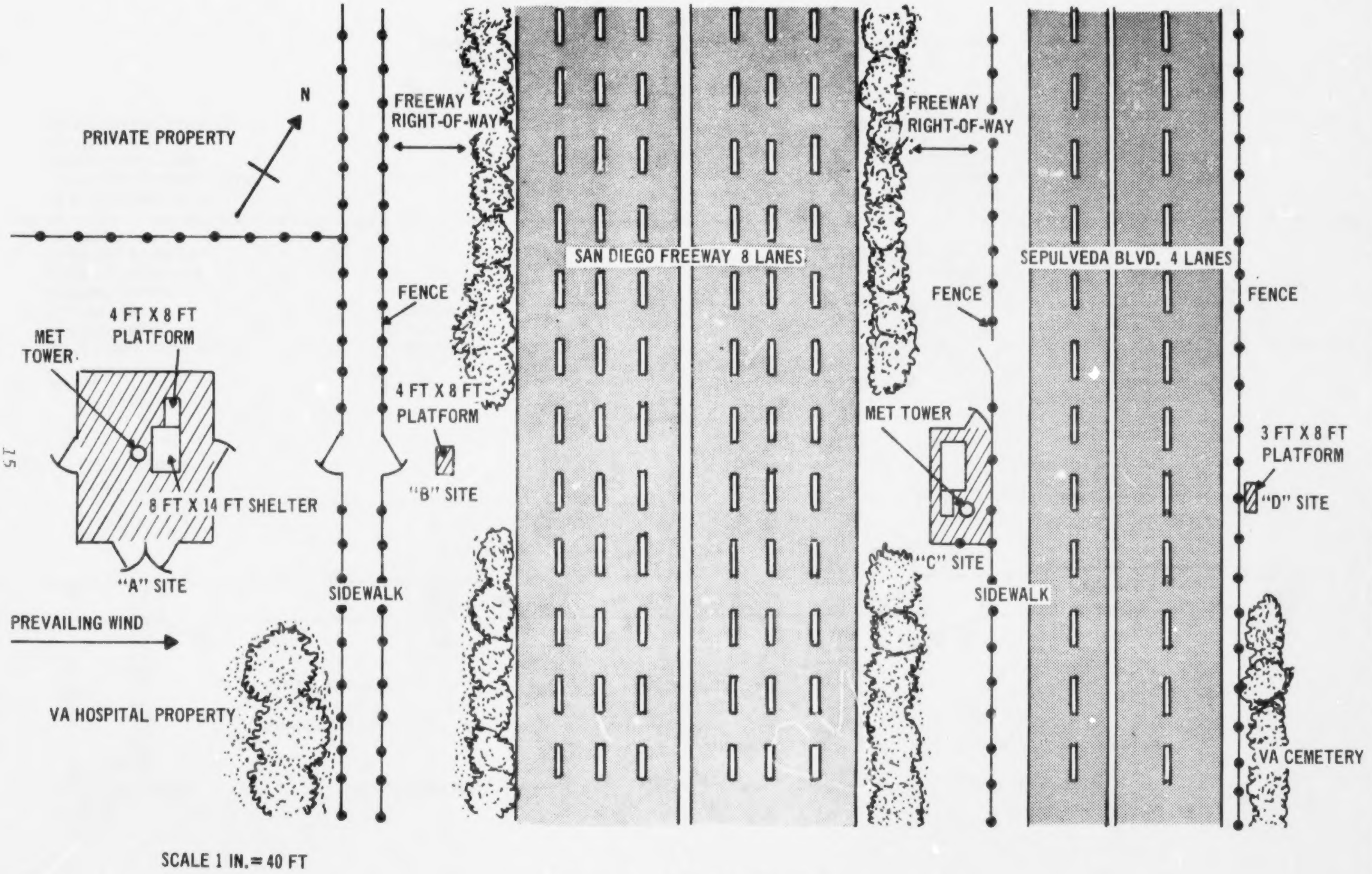
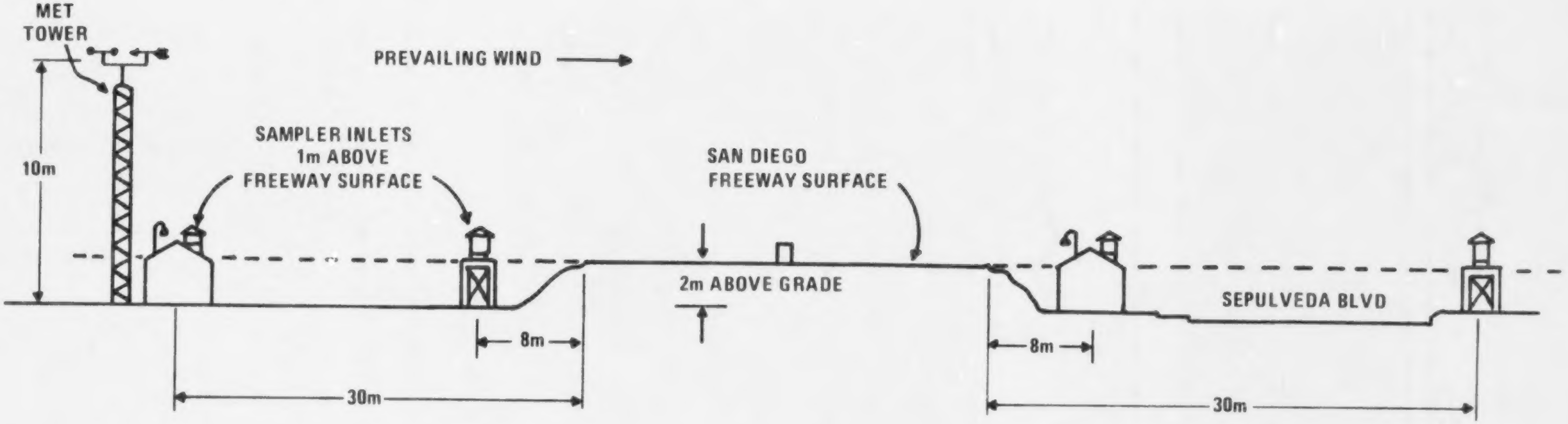

PRIVATE PROPERTY
N
MET TOWER
4 FT X 8 FT PLATFORM
8 FT X 14 FT SHELTER
"A" SITE
PREVAILING WIND
VA HOSPITAL PROPERTY
SCALE 1 IN.= 40 FT
FREEWAY RIGHT-OF-WAY
FENCE
4 FT X 8 FT PLATFORM
"B" SITE
SIDEWALK
SAN DIEGO FREEWAY 8 LANES
FREEWAY RIGHT-OF-WAY
FENCE
MET TOWER
"C" SITE
SIDEWALK
SEPULVEDA BLVD. 4 LANES
FENCE
3 FT X 8 FT PLATFORM
"D" SITE
VA CEMETERY

Figure 3. LACS study site.


MET TOWER
10m
PREVAILING WIND
SAMPLER INLETS 1m ABOVE FREEWAY SURFACE
SAN DIEGO FREEWAY SURFACE
2m ABOVE GRADE
SEPULVEDA BLVD
8m
30m
8m
30m

SITE A

METEOROLOGICAL DATA
24-HR HI-VOL
4-HR HI-VOL
4-HR MEMBRANE
CASCADE IMPACTOR
24-HR SO_2 BUBBLER
CO ANALYZER

BATTELLE IMPACTOR
TOTAL SULFUR ANALYZER
NO/NO_2 ANALYZER
O_3 ANALYZER
DICHOTOMOUS SAMPLER

SITE B

24-HR HI-VOL
4-HR HI-VOL
4-HR MEMBRANE

SITE C

24-HR HI-VOL
4-HR HI-VOL
4-HR MEMBRANE
CASCADE IMPACTOR
24-HR SO_2 BUBBLER
CO ANALYZER

BATTELLE IMPACTOR
TOTAL SULFUR ANALYZER
NO/NO_2 ANALYZER
O_3 ANALYZER
DICHOTOMOUS SAMPLER
TRAFFIC COUNT/SPEED

SITE D

METEOROLOGICAL DATA
24-HR HI-VOL
4-HR HI-VOL
24-HR MEMBRANE

Figure 4. LACS study site composition and elevation.

peak traffic density periods. For comparison purposes, membrane samplers were operated simultaneously with the hi-vols. Andersen cascade impactors were operated on a 24-hour basis to collect information on particle size. In order to obtain long term SO_2 trend data, SO_2 impingers were also operated on a 24-hour cycle. The arrangement of the samplers was so designed to determine the contribution of sulfate/pollutants from the freeway. Particular attention was given to obtaining valid meteorological data and two meteorological stations were installed. The upwind station was instrumented at the 10 meter level. To determine the validity of these measurements, a second station at Site D was operated at approximately the 2 meter level. After it was ascertained that the wind direction data from both stations agreed, the recordings from the downwind site were discontinued.

The samplers listed below the dotted line in Figure 4 were added at Sites A and C during the study period. The Battelle Impactor is operated on an experimental basis to obtain large samples of particulates (>1 gm/day) for possible compound identification work. It collects three size fractions at a flowrate of approximately 25 m^3/min. The two analyzers utilize well proven detection principles: total sulfur is continuously monitored by flame photometric detection, and chemiluminescence is employed by the NO/NO_2 and O_3 instruments. The dichotomous samplers were early models with three channels--fine, coarse, and total. However, only samples from the fine channel were acceptable. The traffic count/speed system became operational in 1976. Both the car count and the speed in 5 intervals is recorded for each of the 8 lanes.

To obtain an estimate of the number of catalyst equipped cars present in the Los Angeles area, sales records and registration are surveyed on a quarterly basis. A satisfactory system to directly identify catalyst equipped cars passing the study site is highly desirable but has been impossible to implement. Since it was know that gasoline in California contains higher concentrations of sulfur (S) than the rest of the nation, fuel samples are being collected and analyzed for S and Pb. The integrated samples being obtained are analyzed by traditional gravimetric, wet chemistry and x-ray fluorescence (XRF) procedures. The data routinely obtained by this surveillance program are shown in Table II.

QUALITY ASSURANCE

To assure the high quality data required for the study, a rigid formalized quality assurance procedure was initiated at the beginning of the study. Integrating samplers are subjected to monthly calibrations and external audit flow checks. Approximately 1% of the integrated samples are analyzed by the contractor and our own laboratory. Blind samples, i.e., filter media spiked with known concentrations of $SO_4^=$, nitrate (NO_3^-), and Pb are sent routinely for analysis to the contractor. The continuous analyzers received daily zero checks, weekly span checks and monthly complete calibrations. Auxiliary equipment such as mass flowmeters and calibrators are checked monthly. As with all phases of the LACS, the quality assurance program has undergone changes during the course of the study. The split and blind sample phase was reduced substantially after the contractor laboratory demonstrated the capability of achieving the desired results. However, since site operation was transferred to contractor personnel in the summer of 1976

TABLE II. LACS DATA BEING OBTAINED - 1/76

Sampling Method	Sampling Interval(s)	Variables Measured
Hi-Vol	3-7 pm & 24 hour	TSP, Pb, NO_3, NH_4, SO_4
Membrane	3-7 pm & 24 hour	TSP, NO_3, SO_4, Al, Br, Ca, Cl, Fe, Pe, Si, Zn, S
Dichotomous	24 hour	TSP, NH_4, SO_4, Strong Acidity, Al, Br, Ca, Cl, Fe, Pe, Si, Zn, S (3 fraction/site-day)
Cascade	24 hour	TSP each stage (6 fractions/ site-date), SO_4, NO_3, Al, Br, Ca, Cl, Fe, Pe, Si, Zn, S on backup filter
Bubler	24 hour	SO_2
Gaseous Analyzers	Hourly	CO, NO/NO_2, Total S, O_3
Meteorology	Hourly	Wind Direction/speed, ambient Temperature/dewpoint
Traffic	5 min Quarterly	Count by lane and speed interval Mix by sales and registration data

the external audit portion has been increased. In addition to ongoing monitoring, numerous studies in the field and in the laboratory have been conducted to determine critical parameters and to evaluate equipment, and where necessary to initiate changes.

REPORTS AVAILABLE

Figure 5 shows graphically the reports available and their relationship to estimated precentages of cars equipped with catalytic converters as obtained from registration information. These precentages do not represent catalyst vehicle miles travelled (VMT). The estimated VMT is approximately 25% to 30%, which was one of the assumptions used in the original EPA estimate for incremental sulfate exposure (Table I). All listed reports pertaining to the period through the close of 1976 are available from the Office of the Director, EMSL. It is hoped that the scientific community will avail themself of these reports and assist those involved in the LACS in making full use of the data base, which as will be shown by the subsequent papers, is extremely well suited for assessing effects on the ambient air quality by mobile source emissions.

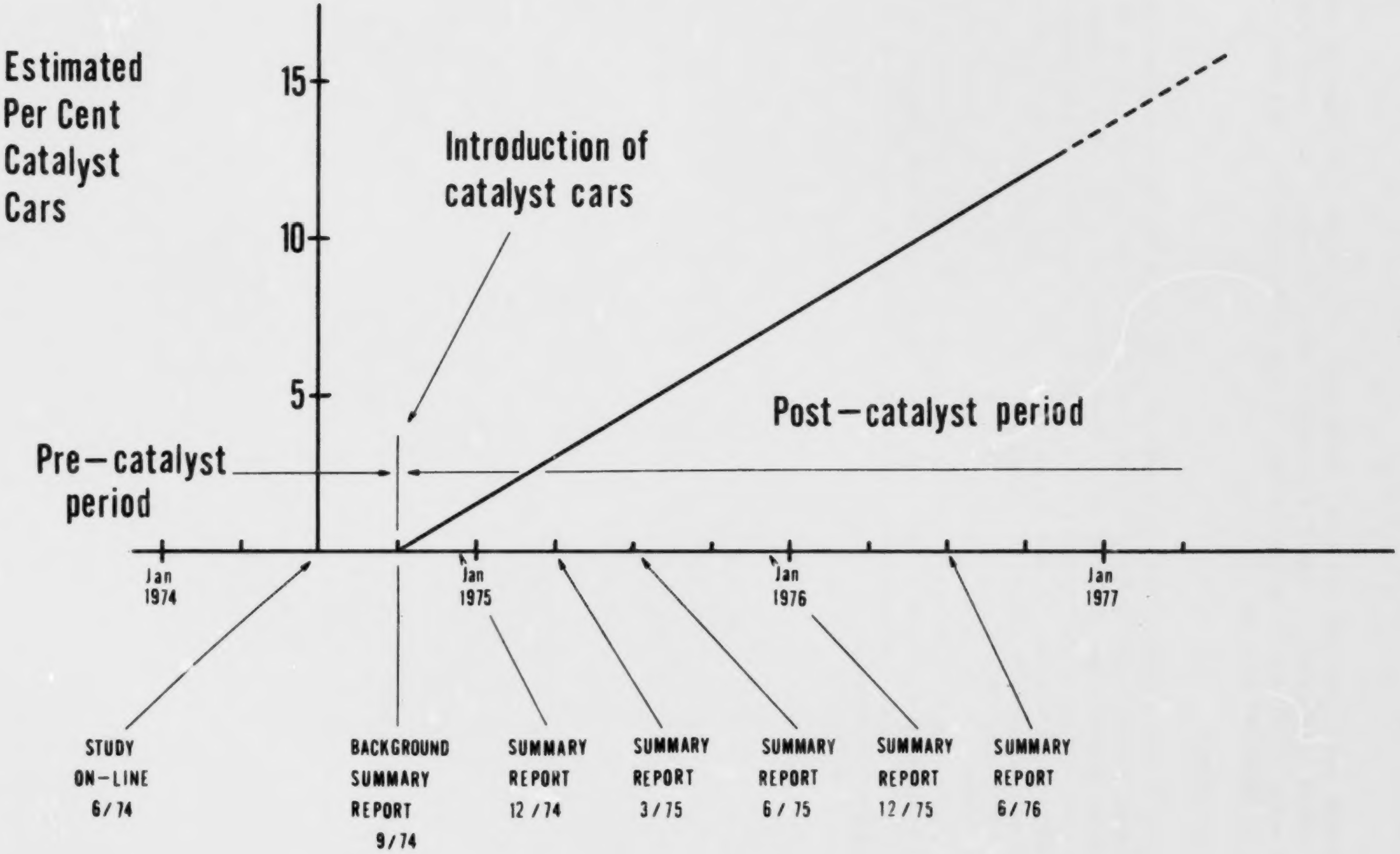


Figure 5. LACS program schedule related to precent catalyst cars.

PREVIOUS SULFATE STUDIES IN THE LOS ANGELES BASIN

Edward P. Parry

Rockwell International
Newbury Park, California

and

Franz J. Burmann

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

During the initial phases of the Los Angeles Catalyst Study, a review of sulfate studies and other pertinent data representing previous work in the Los Angeles Basin was undertaken. This review was prepared at the Air and Industrial Hygiene Laboratory under subcontract to the Rockwell Air Monitoring Center. The results of this review are presented, together with other pertinent information concerning sulfate levels.

The distribution of SO_2 sources in relationship to the Los Angeles meteorology and the Los Angeles Catalyst Study site is discussed. The climatology, general wind patterns, and effect of seasons on general sulfate levels are presented. Maximum two-hour average sulfate levels of 50 to 70 $\mu g/m^3$ have been reported.

A total of 14 air quality studies of the Los Angeles area is identified in the review. Of these, six seemed pertinent to detailed discussion. These studies are presented and discussed as background to the Los Angeles Catalyst Study.

INTRODUCTION

During the early phases of the Los Angeles Catalyst Study (LACS), it became apparent that information on the climatology of the Los Angeles Basin, sulfate levels and their variability in space and time, reliability of previous sulfate measurements, and location of emission sources were most important to the future understanding and interpretation of the data. This information would be important in establishing background sulfate levels and in generally evaluating the site chosen for the study. It would also reveal any previous studies having objectives similar to those of the Los Angeles Catalyst Study and make available the possible conclusions of these studies.

Further, it would help in providing the necessary climatological characterization of the area.

To prepare this review, Rockwell Air Monitoring Center subcontracted with the California Air and Industrial Hygiene Laboratory (AIHL) to search all available sources, select pertinent studies, and evaluate the data and methods employed. By the time this review was underway, initial site selection for the LACS had been completed. The detailed evaluation was, therefore, limited to those studies that included sulfate/SO_2/sulfur measurements performed in areas of high traffic density and geographically related to the LACS site. In addition, only reasonably recent studies were considered, i.e. after 1965, since the methods of measurement of sulfate and sulfur dioxide (SO_2) have significantly changed and improved with time, and the general reliability of the older data might be questioned. A total of 14 air quality studies was identified in the Los Angeles Basin. Of these studies, six were considered pertinent to the LACS and were discussed in some detail. The six studies are listed in Table I. In addition to an analysis of these studies, some information on the emissions from Los Angeles Basin sources and the climatology of the area was also given. In the present presentation, a synopsis of this information is described. The complete report is available from The Environmental Protection Agency (EPA).

SULFUR DIOXIDE EMISSIONS

In 1971, an average of 250 tons of SO_2 per day was discharged into the Los Angeles atmosphere (1). Table II provides a breakdown of these emissions between the various stationary and mobile sources within Los Angeles County.

Of the 250 tons/day total emissions, 210 tons (84%) resulted from stationary sources, principally chemical and metallurgical processing. Sulfur dioxide emissions from power plants are usually of lesser significance but are variable and depend on the availability of natural gas and low sulfur (<0.5%) fuel oil. In Los Angeles County, during the April 15 to November 15 summer months, all utilities are required to burn natural gas when available. During the winter (November 16 to April 14), these facilities are permitted to switch to fuel oil when residential demands exceed gas supplies. During periods of severe natural gas curtailment, daily emissions up to 885 tons of SO_2 have been experienced (1). Any interruption in the availability of low sulfur fuel and natural gas would, therefore, result in increases in SO_2 and particulate emissions.

The major stationary sources are located principally in the industrialized southwestern, south coastal, and the southern portions of the central Los Angeles Basin and the San Fernando Valley areas.

In 1971, approximately four million vehicles moving throughout the Los Angeles Basin contributed about 14% of the total SO_2 emissions, while aircraft contributed about 2% (2). Automotive emissions are generally constant throughout the year with minor seasonal variations, but the diurnal and weekend traffic densities vary markedly.

Sulfur dioxide is formed in the combustion of gasoline from various

TABLE I. LIST OF DATA SOURCES

1. The California State Air Resources Board (ARB) sponsored Aerosol Characterization Experiment (ACHEX) - Rockwell International (G.M. Hidy, Principal Investigator), 1972-73.

2. The ARB sponsored Freeway Aerosol Study (FAS) - University of California, Davis (T.A. Cahill and P.J. Feeney), 1972.

3. The Los Angeles County Air Pollution Control District (LAAPCD), Los Angeles, California, 1965-73.

4. The Federal National Aerometric Surveillance Network (NASN) - EPA, 1965-73.

5. The Federal Community Health and Environmental Surveillance System (CHESS) - EPA, 1972-73.

6. The National Institute of Environmental Health Sciences and EPA sponsored SO_2 to sulfate Conversion Study (SDC) - California Institute of Technology, Pasadena, California (P.T. Roberts and S.K. Friedlander), 1973.

TABLE II. MAJOR SOURCES OF SULFUR DIOXIDE IN LOS ANGELES COUNTY (1971)

Source	Average Daily Emission	
	Tons	% of Total
Chemical/Metallurgical	120	48
Petroleum	55	22
Power Plants	35	14
Total Stationary	210	84
Motor Vehicles	35	14
Aircraft	5	2
Total Transportation	40	16
Grand Total	250	100

Source: Lemke, et al., Reference (2)

organosulfur compounds not removed during refining. Motor fuel (gasoline) can contain up to 0.14% sulfur by weight (3.5 gm/gal). Typical sulfur levels in gasoline sold in California during 1973 are shown in Table III and range from 0.005 to 0.72%. With conventional (non-catalyst equipped) automobiles, virtually all the sulfur in the fuel emerges as SO_2; less than 2% is converted to sulfate before emerging from the exhaust pipe (3,4).

CLIMATOLOGY OF THE LOS ANGELES BASIN

In the Los Angeles Basin during the summer months, subsidence inversions reduce the mixing volume into which the pollutants are dispersed. The average inversion height is about 2000 ft. (600m). In winter, surface inversions are formed by radiative cooling. Although winter inversions occur about three times as often as summer inversions, these are generally weaker and dissipate more quickly during the day. Winter inversions result in higher levels of primary pollutants, such as CO and SO_2, probably because of the lower inversion heights.

During periods of extremely low inversions (surface to 500 ft.), which can occur up to 50% of the time during August through December (5), the pollutants from stationary source stacks can be injected into the atmosphere above the inversion. In such cases, the levels of these pollutants may be abnormally low in the vicinity of the sources and result in abnormally high values some distance downwind when the pollutants reach a region with good vertical mixing.

The daytime onshore wind flow pattern for the Los Angeles Basin under low-level inversion conditions is shown in Figure 1*. At night and early morning, the wind typically reverses direction to blow offshore due to nocturnal radiative cooling (Figure 2). In Figures 1 and 2, the small arrows with the numbers before and after indicate wind variability and average speed. The number behind the arrow indicates the variability class. This is approached in 22½° wind sectors in a 360° wind circle. If 75% of the wind directions fall within a single 22½° wind sector, the wind variability is described as zero. If an additional 22½° wind sector on each side of the original 22½° wind sector (total now 67½°) is required to account for 75% of the wind directions, the variability is described as 1. The addition of another 22½° sector on each side to include 75% is described as 2 (112½° = 2; 157½° = 3; 202½° = 4; 247½° = 5; 292½° = 6, etc.). Double wind arrows imply that the wind occurred nearly all the time from either of the two directions. The average wind speed in miles per hour is also given for each location and is the number in front of the arrow. The onshore wind flow pattern period is longer in the summertime than in the winter. During the summer months especially, the prevailing daytime onshore winds sweep the SO_2 from the major stationary sources generally east inland through the basin.

In Figures 1 and 2, the location of the LACS site is given. As can be seen, favorable winds blow perpendicular to the freeway for extended periods, especially during the summer months. Because these winds blow in from the ocean and no significant sources are in the immediate vicinity, it was

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*Figures 1 and 2 obtained from Reference (6).

TABLE III. SULFUR CONTENT OF GASOLINE IN CALIFORNIA

Gasoline	Sulfur Content - Wt % Average	 Range
Premium		
Southern California	0.034	0.107-0.072
Northern California	0.011	0.006-0.018
Regular		
Southern California	0.046	0.013-0.068
Northern California	0.033	0.005-0.058
Unleaded		
Southern California	0.020	0.007-0.080
Northern California	0.014	-

Source: Shelton E; Motor Gasoline: Summer 1973. Petroleum Products Survey No. 83, U.S. Department of Interior, Bureau of Mines, Bartlesville, Oklahoma (January 1974).

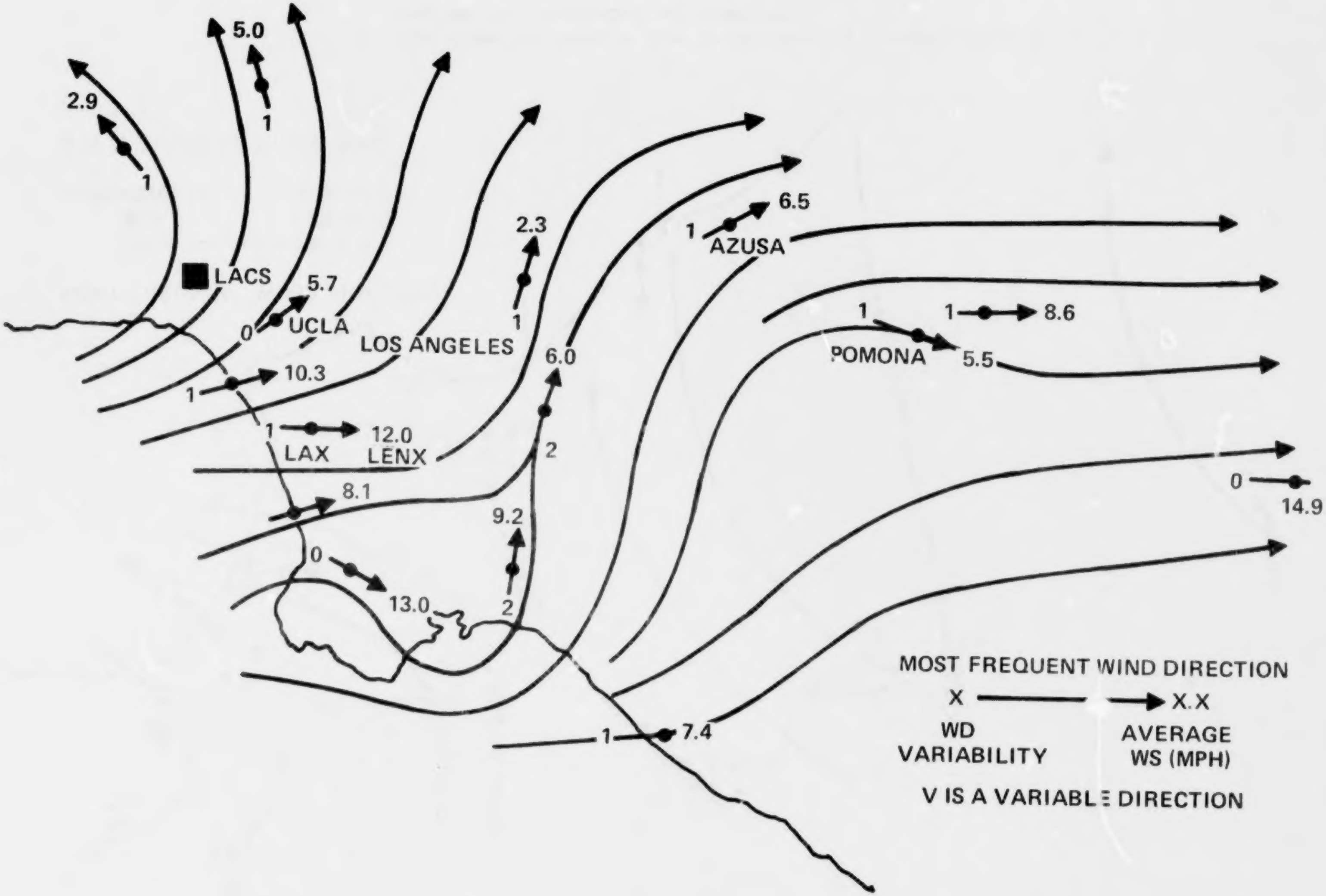
2.9
1
5.0
1
LACS
5.7
0
UCLA
LOS ANGELES
2.3
1
10.3
1
1
LAX
12.0
LENX
6.0
2
8.1
9.2
0
13.0
2
1
AZUSA
6.5
1
POMONA
5.5
1
8.6
0
14.9
1
7.4
MOST FREQUENT WIND DIRECTION
X
X.X
WD
VARIABILITY
AVERAGE
WS (MPH)
V IS A VARIABLE DIRECTION

Figure 1. *Los Angeles Basin - Low level, inversion mean wind flow regime for August at 1200 PST.*

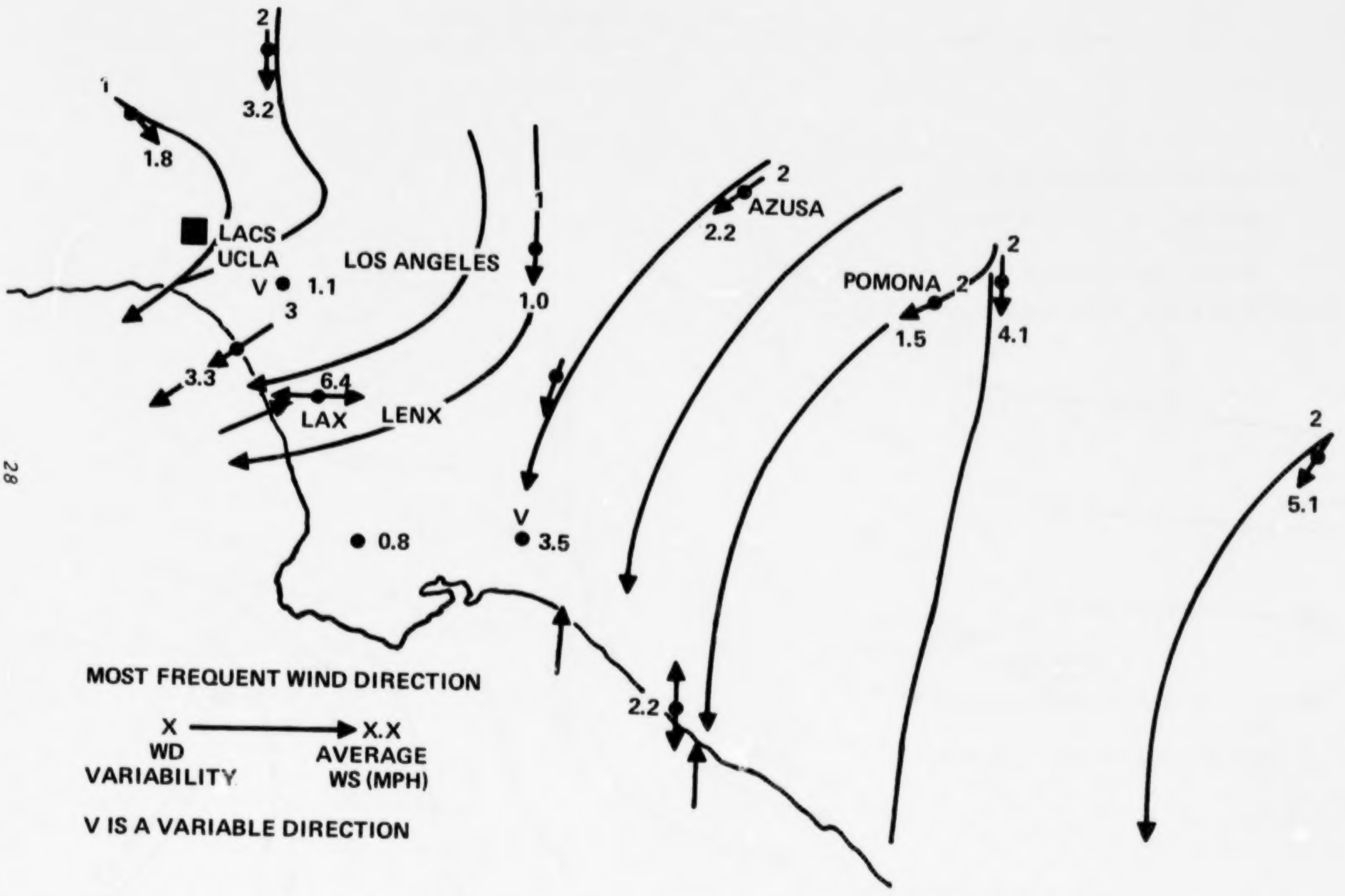
2
3.2
1
1.8
LACS
UCLA
V
1.1
3
3.3
LOS ANGELES
1
1.0
6.4
LAX
LENX
V
3.5
0.8
2
AZUSA
2.2
POMONA
2
1.5
2
4.1
2
5.1
2.2
MOST FREQUENT WIND DIRECTION
X
X.X
WD
VARIABILITY
AVERAGE
WS (MPH)
V IS A VARIABLE DIRECTION

Figure 2. Los Angeles Basin - Low level, inversion mean wind flow regime for September at 0600 PST.

expected that the background sulfate levels would be low. In addition, this portion of the freeway has a high traffic density (∿200,000 cars/day). These factors make the LACS site a favorable location for the study.

As indicated in the introduction, results of six Los Angeles studies were deemed pertinent and were discussed in some detail in the AIHL review. In the discussion below, brief summaries of these studies, including the study sponsor, the objective, a brief description of the results, and an assessment of the measurement methods are presented.

AEROSOL CHARACTERIZATION EXPERIMENT (ACHEX)

This study was sponsored by the California Air Resources Board and was conducted in the summer and early fall of 1972. An additional study was done at the same time of year in 1973. The purpose of the study was to investigate the role of chemical transformation and its relationship to source emissions in the evolution of atmospheric aerosol.

Simultaneous obervations were taken of aerosol properties, gaseous pollutant concentration, and meteorological properties using a mobile laboratory and several fixed stations. Aerosols were collected to obtain as short as two and as long as 24-hour samples for size distribution and chemical composition analysis.

Electron spectroscopy for chemical analysis (ESCA) was used in 1972 as a means of estimating changes in sulfate levels because a sufficiently sensitive method to analyze sulfate in the two-hour filter sample aqueous extracts was not available. ESCA is an analytical technique that can differentiate an "oxidized" sulfur (sulfite and sulfate) from a "reduced" sulfur (sulfur and sulfide). In 1973, a procedure was developed and sulfate data were obtained on two-hour samples by aqueous extraction of the filter and subsequent colorimetric analysis. The pollutant gases monitored included SO_2, hydrogen sulfide (H_2S), ozone (O_3), nitric oxide (NO), oxides of nitrogen (NO_x), methane (CH_4), total hydrocarbons and ethylene and acetylene.

The conclusions from analyzing the 1972 ACHEX data demonstrate that lead (Pb) and bromide (Br) can be correlated well with automobile traffic, but there is no correlation of sulfate levels as measured by "oxidized sulfur." Reduced sulfur, however, correlates well with automobile traffic and is suggested as a traffic indicator. Since two-hour aerosol samples were taken, diurnal plots of gaseous and particulate species were obtained. Figure 3 shows the diurnal variation of several pollutants during sampling at the Harbor Freeway very near downtown Los Angeles. The increased concentrations of lead and bromide during times of high traffic density are obvious. The maximum oxidized sulfur values of 3.5 $\mu g/m^3$ would correspond to a sulfate level of 11 $\mu g/m^3$.

The conclusions reached from the 1973 ACHEX data are:

1. *In most cases, sulfate and SO_2 diurnal peaks occurred at the same time for both SO_2 source-enriched sites and pollutant receptor sites. In no instance did peak SO_2 and sulfate levels correspond to peak Pb concentrations.*

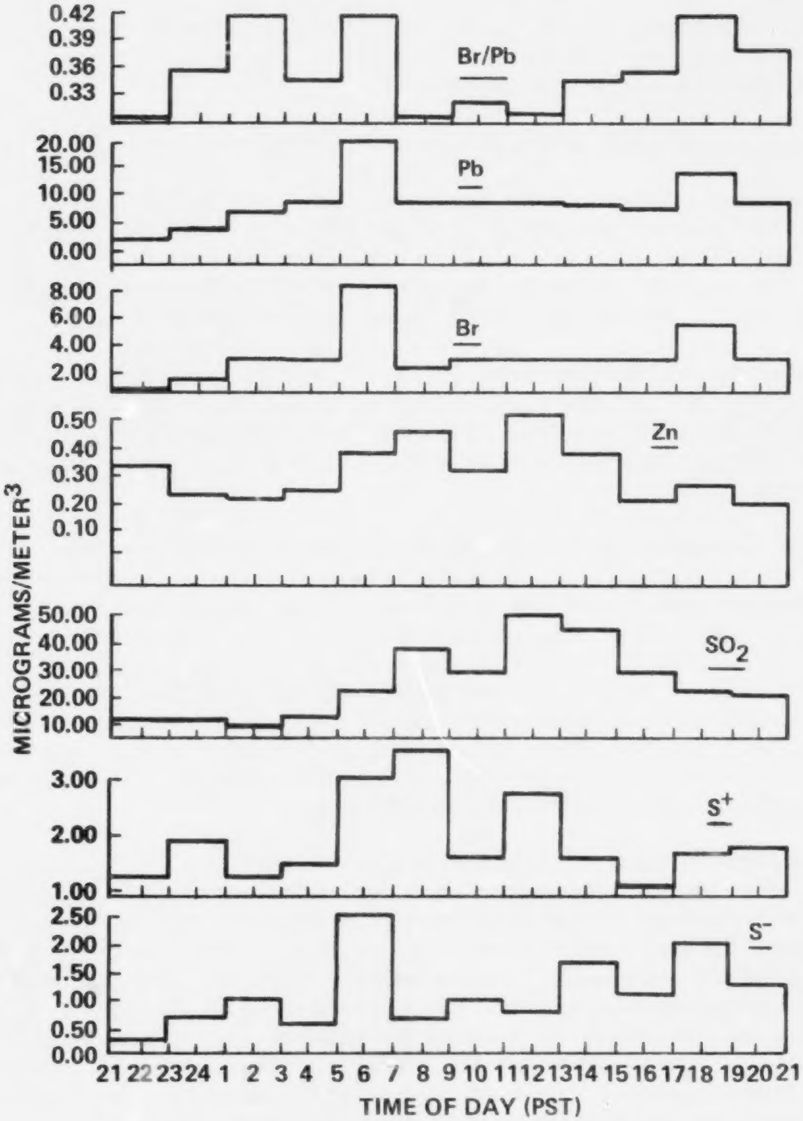

Figure 3. Diurnal patterns for pollutants sampled at the Harbor Freeway on September 19-20, 1972 (ACHEX).

2. The ratio of small particulate sulfate (<0.5 mm) to total particulate sulfate for measurement immediately downwind of major SO_2 sources was small and reasonably constant throughout the day. However, at sites further downwind, the above ratio showed diurnal variations. During the times when total sulfate was a maximum, the small particulate sulfate was large and in one case was 60% of the total.

3. The apparent conversion of gas phase to particulate sulfur was seen to generally increase with distance downwind from SO_2 sources areas.

4. Finally, particulate sulfate levels from 50 to 70 $\mu g/m^3$ were observed as maximum two-hour average values at downtown Los Angeles, West Covina, and Dominguez Hills.

Sampling techniques were validated by comparing results obtained on different samplers. For example, the diurnal total filter (Gelman GA-1 membrane filter) data for sulfate during Phase II composited over 24-hours showed good agreement with sulfate values for 24-hour high-volume (hi-vol) samplers (Whatman 41). During the ACHEX experiment, the 24-hour hi-vol filters were analyzed for sulfate using the turbidimetric method (Intrasociety Committee Method 42401-01-697). The two-hour samples were analyzed for sulfate (in the 1973 experiment) by a method involving the measurement of the change of absorbence of a barium-dinitrosulfanazo III complex in the presence of sample sulfate. The sensitivity of this method is about 2 $\mu g/ml$. Some work was done to validate this method by comparison with other methods. The data showed that at sulfate concentrations of 6 $\mu g/ml$ and above, the agreement with the turbidimetric method was within ± 20%. Data obtained showed that samples analyzed both by ESCA for S^+ ("oxidized sulfur", mostly sulfate) and for sulfate by water extraction did not agree by better than a factor of 2. However, comparison of diurnal patterns for S^+ values and water soluble sulfate values (both samples from the same filter) suggested that the ESCA result can be used in a comparative manner to evaluate relative changes in sulfur levels. X-ray fluorescence analysis was used for analysis of sulfur, lead, bromine and zinc.

FREEWAY AEROSOL STUDY (FAS)

This study was also sponsored by the California Air Resources Board and was conducted by the staff of the Crocker Nuclear Laboratory, University of California (Davis). The purpose of this study was to assess the dispersal of lead (and other emissions) from automobiles, and the relation of these emissions to meteorological conditions and traffic density. This represents the only Los Angeles Basin study known which had as its principal objective the assessment of vehicular emission under ambient conditions. Lead emission was of major interest but other elements were also determined. However, assessment of particulate sulfur emissions from this study is significantly limited, as discussed later. No pollutant gas data were obtained. Four sites on heavily travelled Southern California freeways were used and sampling was done using multistage impactors at various locations both upwind and downwind across the freeway. The rotating stages of the Lundgren impactor permitted two-hour sample resolution. The after filter was also changed on a two-hour schedule. Sampling was conducted during nine days between February and August

1972. In addition to the particulate collection and analyses, simultaneous traffic information and meteorological data were obtained from nearby stations of the California Department of Transportation (Caltrans).

The only analytical technique used in this study for analysis of the particulates on the impaction media and filters was ion induced x-ray fluorescence analysis (IXRFA). Lead, bromine, and sulfur were determined by this technique on the various stages of the Lundgren impactor. For the impactor surface, Mylar covered with a very thin paraffin film was used. Whatman 41 cellulose filters were used as after filters. Interlab and inter-method agreement for Pb and Br were within 10%. The comparative results were obtained for Pb by atomic absorption and for Br by x-ray induced fluorescence. On the impactor stages, the accuracy for sulfur was within 10% for standard samples and within 35% for natural aerosols. The use of a Whatman 41 cellulose filter as the after filter precluded the accurate determination of sulfur because of absorption effects. Thus, sulfur levels were only obtained on the impactor stages. It is estimated that this accounts for only about 50% of the total particulate sulfur. Thus, little can be said about the fate and distribution of automotive particulate sulfur emissions from this study.

A typical data presentation is shown in Figure 4, where the variations of traffic density, wind speed, and lead concentrations collected by the various samplers is given as a function of time during one study period. Inspection of all the data suggests that under some conditions of wind speed, the upwind sampler will show higher lead levels, and the lead levels do not vary uniformly as a function of distance from the roadway. The results suggest that mechanical and thermal turbulence created by the freeway may cause some unexpected effect and that care should be used in designing experiments and interpreting the data.

LOS ANGELES COUNTY AIR POLLUTION CONTROL DISTRICT DATA BASE

As part of its charter to control air quality, the Los Angeles County Air Pollution Control District (LAAPCD) (now called Southern California Air Pollution Control District) has monitored the air in the Los Angeles Basin for a number of years. The LAAPCD data were evaluated to assess the general levels, variability, and distribution of the pollutants of interest. The LAAPCD operates a number of stations in which gaseous pollutants are measured and 24-hour particulate samples are collected with hi-vol samplers. Glass fiber filters are used. These filters are subsequently analyzed for sulfate, lead, and other pollutants. A turbidimetric method was used for the sulfate analysis, while atomic absorption analysis was used for lead and zinc. Carbon monoxide was determined by non-dispersive infrared analysis and sulfur dioxide was determined by continuous conductometric analyzers. In Figure 5, the pattern for the annual averages for the 1966-1973 periods are given for several pollutants. The S_p/S_g value is the ratio of particulate sulfur to gas phase sulfur. The mean sulfate value for the period 1966-1972 for West Los Angeles is 7.8 $\mu g/m^3$. For downtown Los Angeles, the mean value is 13.1 $\mu g/m^3$ and for Lennox 11.9 $\mu g/m^3$. The slope of the plot is positive with recent values in the 11-16 $\mu g/m^3$ range. Monthly arithmetic mean plots of the LAAPCD data indicate that the peak sulfate values occur more often in the summer months, suggesting that the higher solar irradiation at that time of year gives

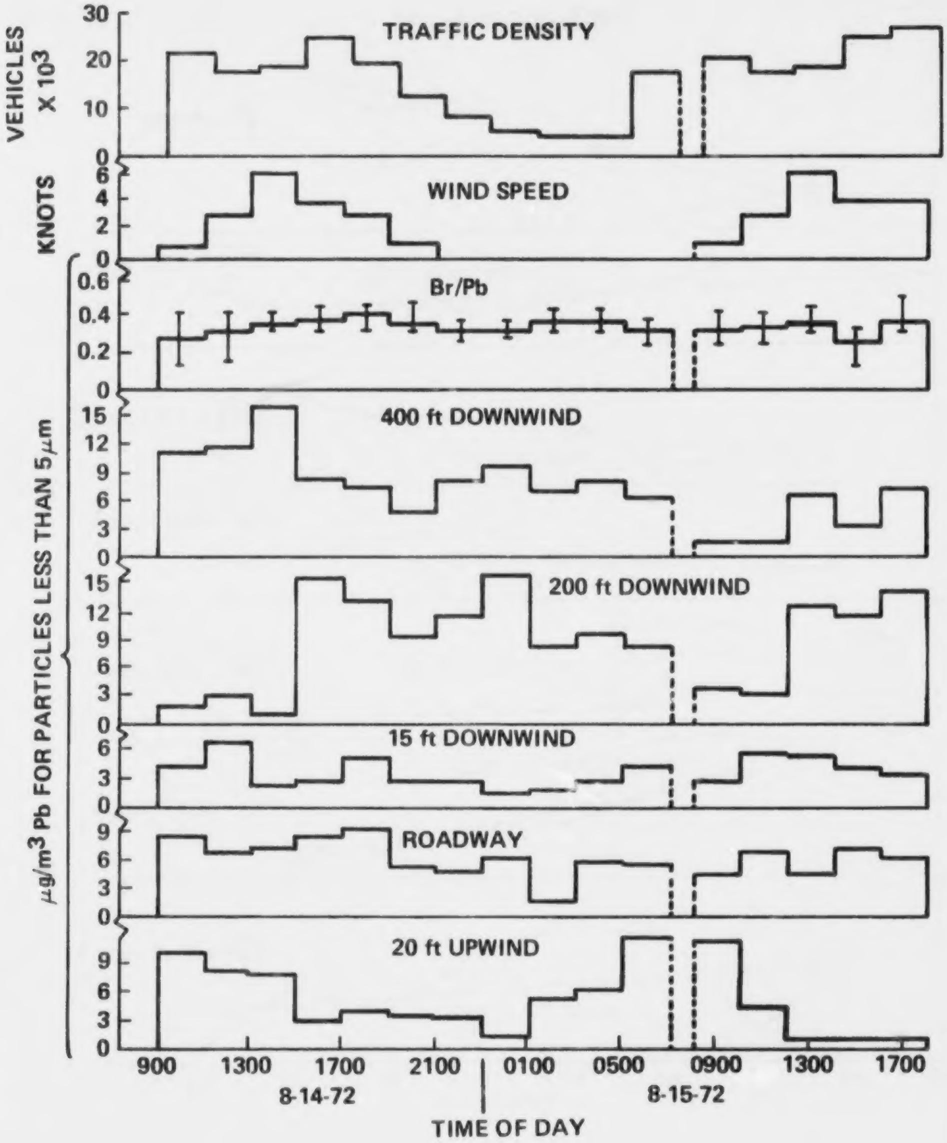

Figure 4. Diurnal variation in lead by impactor location at San Diego Freeway on August 14, 1972 (Freeway Aerosol Study).

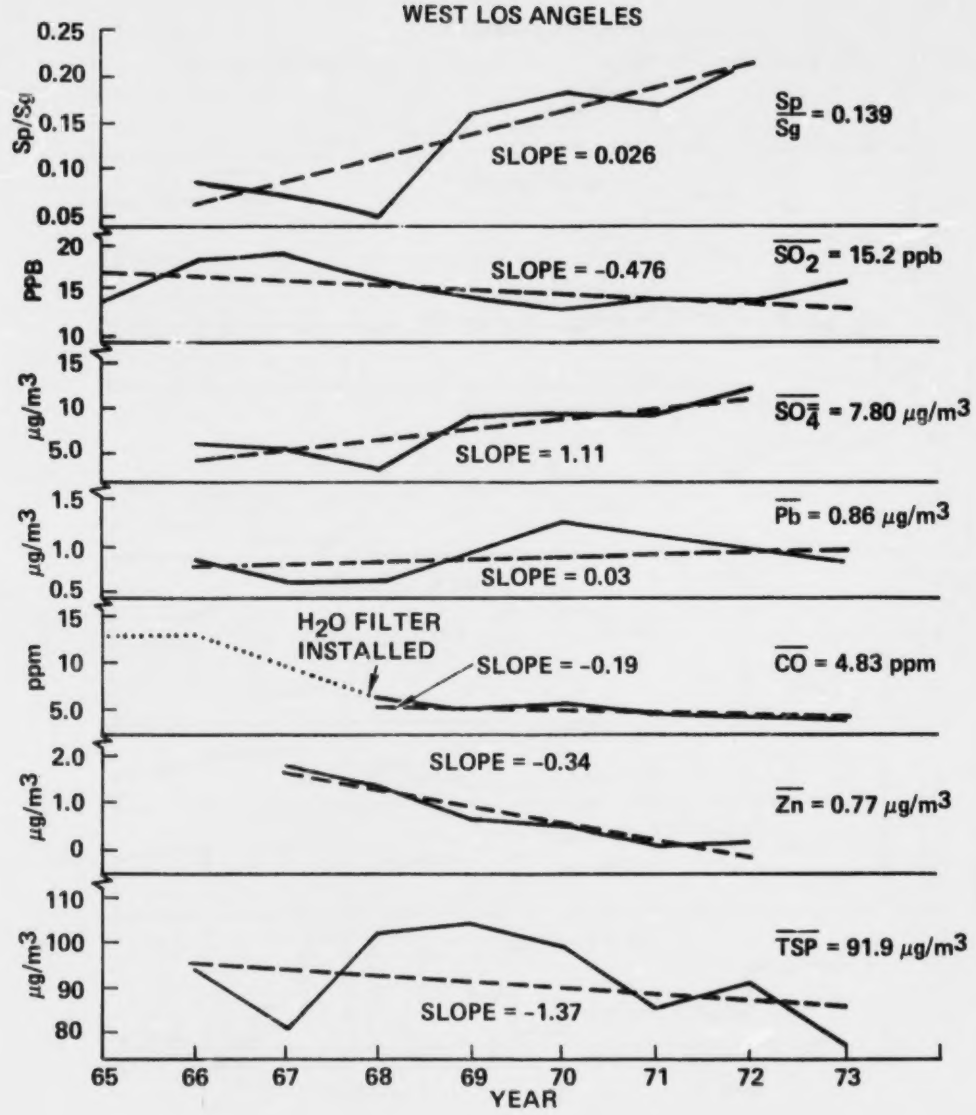

Figure 5. Pattern of annual averages for West Los Angeles from Los Angeles County Air Pollution Control District Data.

rise to a greater photochemical oxidation of SO_2 in the presence of the other atmospheric pollutants. Plots of other pollutants [carbon monoxide (CO), Pb, SO_2 and total suspended particulates (TSP)] also show cyclical behavior with maxima generally in the winter months. This is probably caused by low level winter inversions and the winter use of fuel oil in the basin.

NATIONAL AEROMETRIC SURVEILLANCE NETWORK DATA BASE

The National Aerometric Surveillance Network (NASN) is operated for surveillance purposes by the U.S. Environmental Protection Agency. Comparison of annual averages of TSP, sulfur dioxide, and sulfate with the previous LAAPCD data are of interest. In Figure 6, plots of the annual average for TSP and sulfate are given using both NASN and LAAPCD data. The two samplers were immediately adjacent to each other, but operated on different schedules. Significant differences exist between the two sets of data. For sulfate, the NASN data show essentially a constant concentration while the LAAPCD data show an increasing concentration. The analysis of sulfate by the Environmental Protection Agency for the NASN project has been done by the methylthymol blue method.

Although the NASN sampling schedule was different from that of the LAAPCD, the sample collection data coincided on 22 occasions for the 1965-1972 period. Figure 7 shows a scatter diagram for those comparative results. Some large discrepancies are evident. Analysis of the data shows that the values reported by NASN are on the average 19% greater than the LAAPCD results for these 22 days of side-by-side sampling. Even though there were differences in analytical method, sampling technique, high-volume flow calibration procedure, type of filter, 24-hour sampling schedule, and sampler flow rates employed during sampling, it is still difficult to propose a completely rational explanation of these differences in the data.

COMMUNITY HEALTH AND ENVIRONMENTAL SURVEILLANCE SYSTEM DATA BASE

The Community Health and Environmental Surveillance System (CHESS) was operated under contract by the U.S. Environmental Protection Agency. The objective of the study was to relate pollutant levels to human health effects. A number of stations were located throughout the Los Angeles Basin in which various gaseous pollutants (including SO_2) and particulates were measured. The 24-hour high-volume sampler with glass fiber filter was used to collect particulate samples. Sulfate was analyzed using the turbidimetric method. From CHESS data, based on analysis of 128 samples in triplicate, a precision of ± 5.8% at the 95% confidence level, and an accuracy, based on standard addition, of ± 11.2% was reported. However, differences of up to 430% have been found for analysis of two different strips of the same high-volume filter when analyzed by the CHESS contractor and the New York City Air Pollution Control District.

One of the CHESS stations was in Santa Monica, which is four miles east of the West Los Angeles station of LAAPCD. In 1972, the average of 8 months (from May through December) CHESS data for sulfate gave a value of 8.4 $\mu g/m^3$. The West Los Angeles station of the LAAPCD gave an annual average for 1972 of about 12 $\mu g/m^3$. However, in 1972 some rather high sulfate levels were

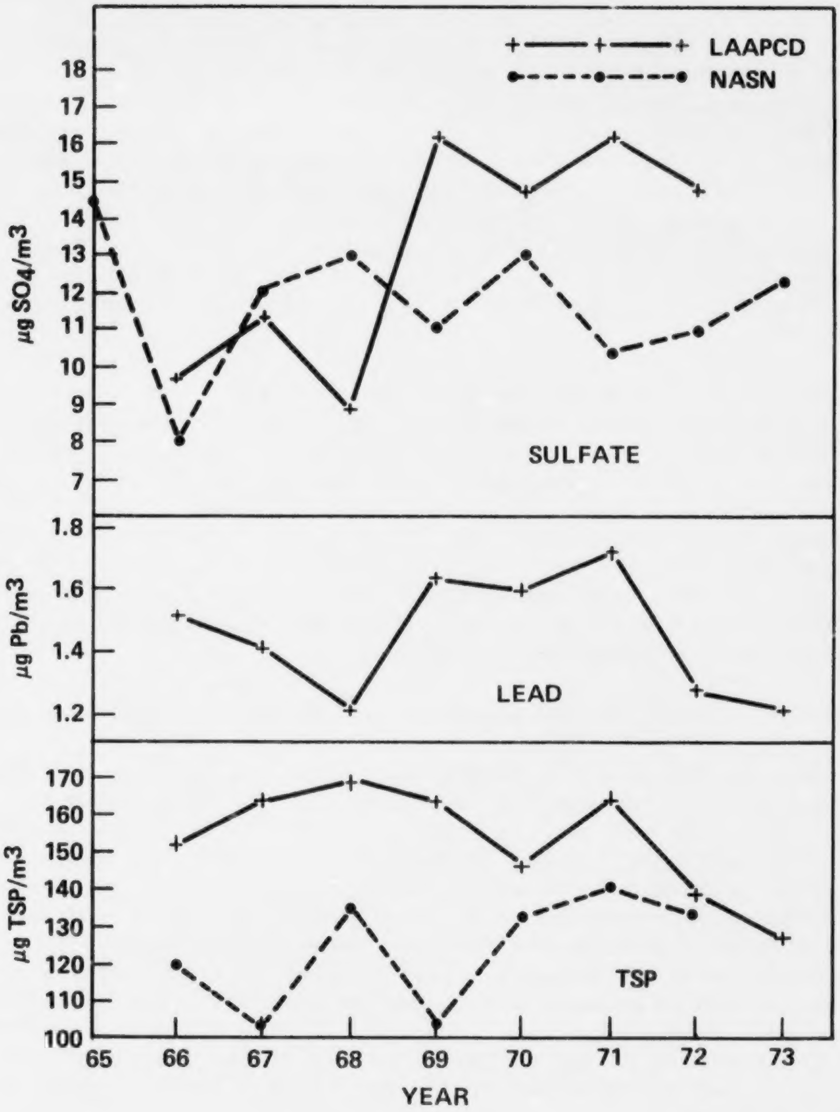

Figure 6. Comparison of LAAPCD and NASN data from downtown Los Angeles location: stations are immediately adjacent.

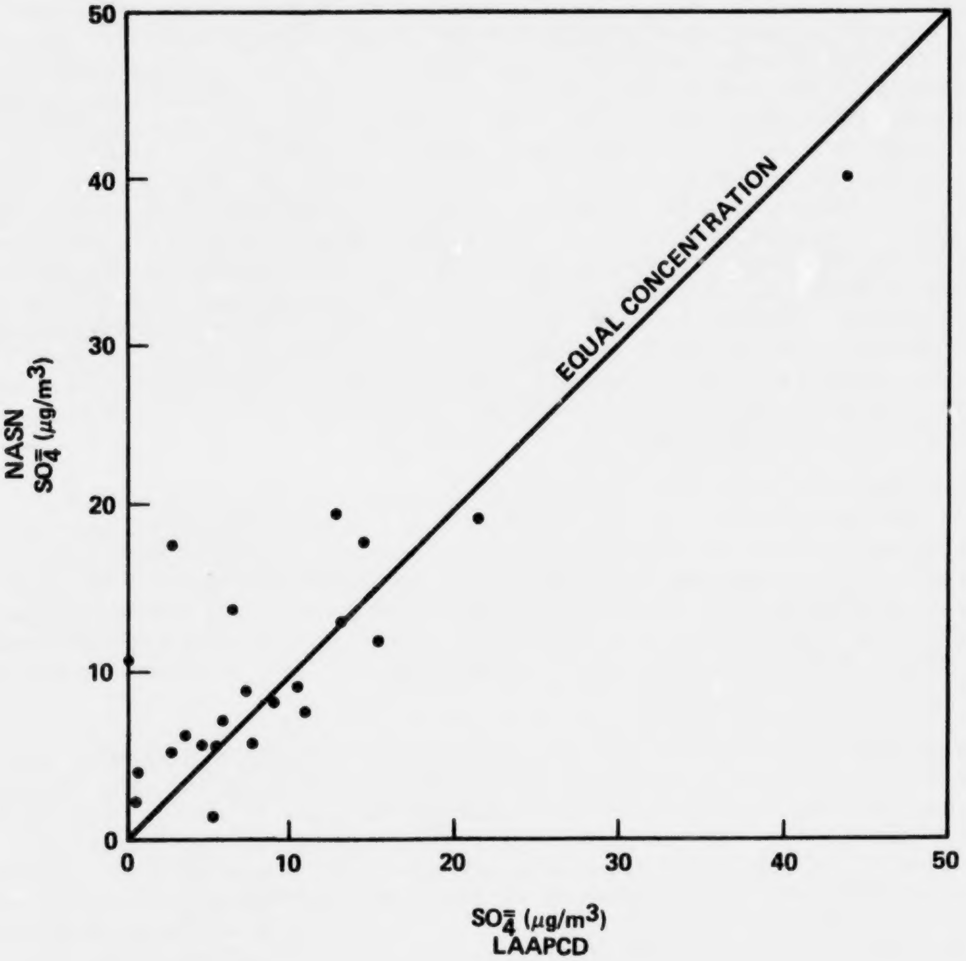

Figure 7. Comparison of paired sulfate concentrations reported by LAAPCD and NASN

measured during the first of the year. Comparison of data covering the same period of time show about a 20% difference between the two sets of data. Fairly good agreement was also obtained between TSP values determined in the CHESS program and by the LAAPCD.

SULFUR DIOXIDE CONVERSION STUDY

The Sulfur Dioxide Conversion Study (SDC) was conducted in 1973 by the California Institute of Technology, Department of Environmental Engineering Science. It was conducted to determine the conversion rate of SO_2 to particle phase sulfur (sulfate) in urban atmospheres. In this program, gas phase sulfur and particulate phase sulfur concentrations were measured in the Los Angeles Basin near major stationary sources and at a downwind receptor site. Measurements of SO_2 and sulfate were made on five days generally coinciding with measurements made during the 1973 Aerosol Characterization Experiment (ACHEX) (see earlier). The SO_2 measurements were made with a continuous flame photometric analyzer. For the sulfate analysis a new technique was developed at the California Institute of Technology wherein particulate was collected on a glass fiber filter. The filter, after collection, was heated to 1100°C and the emitted gaseous sulfur species was determined by a flame photometric detector. Since data were obtained for the same time period and in the same location for this study as for the ACHEX study, comparison of this method with the ACHEX wet chemical sulfate method could be made. Comparison shows that the new method gave low results consistently with differences as high as a factor of 2. However, the diurnal patterns obtained in the two studies were similar.

From the collected data, Roberts and Friedlander (7) were able to estimate the apparent rate of SO_2 conversion in the Los Angeles Area. For this, the LAAPCD data for SO_2 along wind trajectories between source-enriched sites and Pasadena, the average ratio of particulate to total sulfur (gas phase and particulate) at Dominguez Hills and Pasadena, and the estimates of additional SO_2 inputs along the trajectory were used. The values obtained ranged from 1.2 to 13.0%/hour with a mean value of 7.2 ± 3.8%/hour based on data for three days in July 1973.

An additional aspect of the SDC study was an effort to determine the influence of auto exhaust catalytic converters on sulfate levels near roadways and at the receptor site, Pasadena. Assuming all cars to be equipped with catalytic converters, 50% conversion of sulfur in gasoline to sulfate by each car, and gasoline containing an average of 0.075% sulfur*, an increase of 76 $\mu g.m^3$ $SO_4^=$ above the levels due to other sources was calculated by these investigators "near freeways at rush hour". About a 10% increase in sulfate level was calculated for a low traffic density area (Pasadena) after two model years of catalytic converter use.

CONCLUSIONS

The AIHL review has assembled information on the sulfur dioxide emissions in the Los Angeles Basin, the climatology of the Los Angeles Basin, and the

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*This is an upper limit to the sulfur content found in South Coast Basin gasoline.

results of several sulfate related studies performed in portions of the basin. Data are given indicating that in 1971 84% of the SO_2 in the basin came from stationary sources and 14% came from vehicles. About 2% came from aircraft.

The climatology of the area is characterized by subsidence inversion in the summer months with an average inversion height of about 600 m. Surface inversion occurs in the wintertime but generally dissipates quickly during the early day. Winter inversions generally give rise to higher concentrations of primary pollutants (CO, SO_2). The summer low subsidence inversions give rise to reduced mixing volumes for extended periods of time and, with the increased solar radiation, result in much higher concentrations of secondary pollutants, including sulfate. During the day the prevailing wind is off the ocean and at night it is generally off the land. The period of time in which the flow is off the ocean is longer in the summer than in the winter.

The location of the LACS site is shown to be favorable, having extended periods when the wind is perpendicular to the freeway (especially during the summer) and having high freeway traffic density. The background sulfate is also expected to be low on the basis of stationary source locations.

The results of the six previous studies which were evaluated indicate that in some areas of the Los Angeles Basin, east of the sources, the maximum two-hour average sulfate level can reach 50 to 70 $\mu g/m^3$ in the summer. In West Los Angeles near the LACS site, the average value is in the 7-14 $\mu g/m^3$ range, although significant discrepancy exists in the past data.

One study was done to relate ambient pollutant concentrations (mainly lead) to traffic emissions. The results suggest that mechanical and thermal turbulence can cause unexpected effects when monitoring near freeways.

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DISCUSSION

My name is Pierson, Ford Motor Company.

Mr. Trakowski has recounted the events leading to the project we are here to discuss. He noted that about 4 years ago was the time of origin of concern about sulfuric acid from catalyst-equipped cars. He said he was not sure who it was who first expressed concern---"

The information is in the record of the EPA resuspension hearings conducted by Eric Stork in 1975. It was Ford Motor Company who first expressed concern. The problem was discovered in 1972 in my lab at Ford on samples obtained from Dow Chemical Company. As to how notice of the problem was given: I informed Otto Manary at Dow in a letter Dated October 20, 1972. Herbert L. Misch informed the EPA in a letter of February 1973.

The detailed story has been given in a number of publications. I would like for this to appear in the record of this meeting.

SELECTION RATIONALE FOR ANALYTICAL METHODS FOR THE LOS ANGELES CATALYST STUDY

Richard J. Thompson

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The first considerations in the selection of analytical methods were the data needed and the sampling that could be implemented. Upon consideration of the data output and the monitoring strategy, the methods were selected on the basis of reliability [considering both reproducibility and repeatability], precision [with standards and with real samples], training [technology transfer], and cost [time, equipment, and personnel]. The analytical methodologies to be employed were to be fitted within the framework of a quality assurance program and implemented by contract personnel in more than one contract laboratory.

INTRODUCTION

My distinguished colleague has described to you the objectives of the Los Angeles Catalyst Study (LACS) and the information needed to attain these objectives. This presentation is given to outline the rationale for selecting analytical methods, the two prime governing factors being accuracy obtainable and practicalities imposed.

PROCEDURES

The first consideration in such a selection, of course, is the nature of the data needed and the sampling that can be implemented. To obtain the data output necessary from the samples obtained, factors used in selection for the LACS were: reproducibility (within a laboratory); repeatability (between laboratories); precision (obtained with standards and with environmental samples); technology transfer (training of contractor personnel); and cost (time, equipment and personnel). Implementation of a quality assurance program was essential. These factors are summarized in Table I.

Ideally, one has inter-laboratory standardization data upon which to base judgment (and from which standardized methods can be secured) and one has standard samples for an audit program. The only body of available knowledge of the type necessary at the time of initiation of the LACS study consisted of unpublished information gained by experience and based on published methods not subjected to formal or structured comparisons. The methods are shown in

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TABLE I. GOVERNING FACTORS: ACCURACY AND PRACTICABILITIES SELECTION CRITERIA (AS OF FEBRUARY 1974)

Parameter	Desired	(Other Than Journals) Obtainable
Reproducibility	Intensive Ruggedness Testing	EMSL Experience
Precision	SRM's	Lab Reports
Repeatability	Inter-Laboratory Comparisons	Informal Sample Splits
Methods	Standardized Methods	In-House Write-Ups
Standards	SRM's	Commercial/Internal
Technology Transfer	Formal Courses	EMSL
Quality Assurance	Standardized Programs	In-House Quality Control and Sample Splits

Table II. They had been employed internally for thousands of samples, and information had been painfully accrued as to what readily identifiable mistakes could be made routinely, how they could be avoided or minimized, and how effective internal quality control could be effected.

In the main, the methodologies used internally, including quality control procedures, were implemented by two prime mechanisms: documents and personal contact. The documents included published and in-house texts; personal contacts included training in Environmental Monitoring and Support Laboratory (EMSL) labs and verbal interchange by telephone.

The methods used have been subsequently investigated extensively elsewhere and found to be state-of-the-art methods, with some exceptions.

Quality assurance will be presented later, but, as summarized in Table III the following steps were taken:

Special filters were supplied by EMSL which had been obtained to specifications.

Sample splits with EMSL were imposed at a high level (10%). Discrepancies were noted and corrected in the case of sulfate and nitrate; the ammonium ion had and has been proved to be elusive in the samples obtained. (As will be mentioned later, blind audits were initiated when samples became available.)

The internal checks used by EMSL were adopted routinely by the contractor lab, and included incorporation into the samples sets: open and blind duplicate strips of randomly selected samples; standards for each nth sample; and spiked duplicates. Automatic re-runs are made of samples containing over a pre-set level of a component. Overall, over a quarter of the analytical burden is for quality control.

As a specific example, the case of platinum was of interest. Platinum, a possible environmental contaminant of hazard to human health was considered, and the following was needed to assess the potential problem.

- *The environmental level had to be determined.*
- *A method had to be demonstrated on real samples.*
- *A rountine method had to be proven for environmental samples.*

In an elemental survey of particulate matter, platinum was found at some 4×10^{-11} g/m^3 *by SS/MS, which was very imprecise. The geochemical levels were anticipated to be found in particulate from ambient air (some* 2×10^{-12} g/m^3*) using the geochemical platinum content and an average ambient TSP assumed to be of the same platinum content. As was stated in an in-house report, "the positive analysis of ambient air for noble metals is anticipated to be quite challenging, if indeed possible."*

A massive sample was obtained from a public building near the LACS site. The 1.5 kg sample contained a considerable amount of non-suspended particulate matter, such as beetles, etc.

TABLE II. METHODS CHOSEN (FEBRUARY 1974)

Parameter	Sample Preparation	Analytical Method
Lead	(LTA +) Acid Digestion	Atomic Absorption
Nitrate	H_2O Reflux	Colorimetric (Cu/Cd, Griess-Ilsovay)
Sulfate	H_2O Reflux	M T B
T S P	Conditional 72 ± 1^0F & 45 ± 5% RH	Mass
SO_2	--	Bubbler/West-Gaeke

TABLE III. INITIAL QUALITY ASSURANCE

- Analyzed Filters Bought to Specifications Furnished
- Duplicate Samples Were Run By EMSL and Contractor (10%)
- EMSL Quality Control Procedure Furnished, Contractor QAB Plan Examined
  - Duplicates (open and blind)
  - Standard Every Nth Sample
  - Spiked Duplicate
  - Automatic Rerun of Values Over a Selected Level

The sample was homogenized and halved. One half was spiked with known stable isotopes of platinum, palladium, and ruthenium (a suitable isotope of rhodium was not available) and oxidized in a muffle furnace with incremental temperature increases programmed. The residue was dissolved in analyzed aqua regia; a known gold carrier added; and the precious metals obtained by reductions with zinc. The gold button bearing the precious metals was dissolved in analyzed aqua regia, diluted to volume, and aliquots distributed to participating laboratories. The aliquots were analyzed by EMSL, Stewart Labs, and Battelle Northwest.

RESULTS

The information obtained is given in Table IV. Fortunately, soluble platinum species were not identifiable in catalyst equipped automobile effluents, and adverse biological effects have not been noted. A routine method for platinum at atmospheric levels does not appear existent nor obtainable at the current state-of-the-art.

TABLE IV. ENVIRONMENTAL PLATINUM

Sample	Method	Pt Level (g/m^3)
Suspended Particulate Method	SS/MS	4×10^{-11}
Geochemical [1]	Literature	2×10^{-12}
Massive Sample [2]	IDMS	$2\text{-}5 \times 10^{-12}$
	NAA	$<9 \times 10^{-11}$
	AAS	$<3 \times 10^{-11}$
	XRF	NS
	OES	NS

[1] An average Los Angeles particulate loading was assumed to contain platinum at the average geochemical level given in the literature.

[2] An air volume was assumed from the average Los Angeles particulate loading and the mass of the sample.

DETERMINATION OF LOW CONCENTRATIONS OF PARTICULATE NH_4^+ WITH THE SPECIFIC ION ELECTRODE

Lloyd S. Shepard, George Colovos, and Allen M. Miles

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The development of a method employing an ion sensitive electrode and the Gran-plot for the microdetermination of NH_4^+ in particulates will be discussed. For the successful application of this method without loss of NH_4^+ as NH_3 during the determination, addition of a small amount of NH_4^+ (about 0.1 ppm) to the recipient solution is necessary. Response of the electrode and the slope of the Nernstian plot should be determined carefully before use of the method. These experimentally determined electrode parameters should be used for the Gran-plot rather than theoretical values to avoid erroneous data. The sensitivity, precision and accuracy of the developed method are given and comparisons between this method and the automated indophenol method are discussed. Results of analyses of both synthetic and ambient samples are presented.

INTRODUCTION

Several papers presenting applications of the ammonia sensitive electrode have been published. T. R. Gilbert and A. M. Clay (1) first and later R. F. Thomas and R. L. Booth (2) studied its application to the determination of ammonia in water and wastewater samples. J. M. Bremner and his co-workers (3,4) have used electrodes for the determination of ammonia in soil extracts and others (5,6) have used them for ammonia determination in the presence of urea. In all the above studies, the electrode response is directly proportional to the logarithm of the concentration. This approach is quite acceptable for relatively high concentrations, but for low concentrations it is somewhat difficult to apply direct potentiometry because the electrode response becomes too slow to reach the equilibrium potential at a reasonable time. This problem can be minimized by utilizing a standard addition technique, thus decreasing the response time of the electrode.

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In addition to the faster response of the electrode, the standard addition method offers the advantage of applicability to the Gran-plot technique (7) for the estimation of the amount of ammonia present in the sample. The Gran-plot technique is based on the linear extrapolation to zero of a plot of the exponential form of the Nernst equation. This in the case of the ammonia sensitive electrode is given by equation 1

$$[NH_3]_a = k \cdot 10^{-Em/S} - [NH_3]_o \qquad 1$$

where k is a constant related to the normal potential (E_o) *and the slope of the electrode response,* E_m*, is the measured potential,* $[NH_3]_o$ *and* $[NH_3]_a$ *are the original and the added concentrations of ammonia, and S is the slope of the electrode response.*

This combination of standard addition and Gran-plot techniques has been used by several investigators in connection with various ion sensitive electrodes, such as fluoride (8,9), cesium (10), lead (11) and others. Most recently, W. Selig, J. W. Frazer and A. M. Kray (12) have used this approach for the microdetermination of ammonia with an ammonia sensitive electrode titration system interfaced with a minicomputer. With this system they were able to determine accurately ammonia in the range of 28 ppb to 2.8 ppm of ammonia nitrogen. The manual version of the above technique has been investigated by us and, through these studies, we were able to develop a method for the determination of submicrogram amounts of ammonia in solution. The developed method was then applied to the determination of particulate ammonium collected with the aid of a dichotomous sampler on 37 mm Teflon filters.

In this paper, the result of our studies are reported.

EXPERIMENTAL

INSTRUMENTS AND APPARATUS

An ammonia selective electrode (Orion M-95-10) connected to a Beckman Expandomatic SS-2 pH meter was used throughout this study. The sensitivity of the SS-2 pH meter was increased greatly through the use of a Heathkit (EU-200-01) amplifier connected with a Heathkit (EU-200-02) potential off-set module by which the signal could be appropriately offset and amplified to be recorded on a strip chart recorder.

All the titrations were conducted in a thermostated, specially constructed glass cell. The temperature of the titration cell was kept constant by circulating water from a constant temperature water bath (Haake, Inc. Model FJ).

REAGENTS

All chemicals were Baker analyzed reagents unless otherwise specified. Ammonium chloride solution (0.1N) was prepared by dissolving 5.3 g NH_4Cl *in a liter of water. Stock solution of ammonium (1000 ppm* $NH_3 \cdot N$*) was* *prepared by dissolving 3.82 g of NH_4Cl in a liter of water. The working standard (100 ppm $NH_3 \cdot N$) was prepared by diluting 10.0 ml of the solution to a liter with ammonia free distilled water. The conditioning solution was prepared by diluting 2.5 ml of the working standard solution to a liter with ammonia free distilled water. Solutions of 0.1 or 2.5N NaOH and 1.0N HCl were prepared by diluting appropriately concentrated solutions of NaOH and HCl, respectively.*

PROCEDURE

The ammonia electrode must be kept in solution at all times. Between titrations, the electrode was kept in a solution of 0.1N NaOH. When it was not in use for any extended period of time, the electrode was stored in a solution of 0.1N NH_4Cl. Each time the electrode changed solutions, it was rinsed thoroughly with distilled water and wiped dry with a Kimwipe. Care was taken not to damage the hydrophobic membrane. Membrane damage can be detected from the electrode response time. The response of electrodes with damaged membranes is usually very slow.

The procedure requires independent, accurate determination of the slope of the Nernstian response of the electrode. This was accomplished by adding 5.0 ml of distilled water spiked with 10 μl of 1.0N HCl into the titration vessel, covering with a sheet of parafilm and stirring the solution for approximately five minutes. After this, the electrode was removed from the 0.1 NaOH (kept at room temperature, 22°C-25°C), washed well with distilled water, dried with a clean Kimwipe, and placed in the titration vessel, making sure there were no air bubbles trapped on the electrode membrane. The desired levels of ammonia in the solution were obtained by adding small (μl) volumes of working standard into the solution with the aid of a micropipet. Initially, 5.0 μl of working standard was added and the solution was stirred for one minute. 0.5 ml of 2.5N NaOH was then pipetted into the titration vessel, and the potential recorded until the change in potential for a one minute time interval was less than 0.5 millivolts. This amount of change defines a plateau in the voltage vs time plot. Another 5 μl of working standard was added and the new potential was measured again at the plateau. The addition of ammonia was continued in increments of 5 μl until a stable potential reading for 180 nanomoles was obtained. From these data the slope of the Nernstian response of the electrode was determined by plotting the measured potentials against the logarithm of the corresponding ammonia concentration. The concentration of ammonia in the conditioning solution (blank) was determined as follows:

Two ml of the conditioning solution (0.250 ppm $NH_3 \cdot N$) and then 10 μl of 1.0N HCl were added into the titration vessel. The solution was then stirred for approximately two minutes, and then 3.0 ml of distilled water were added. The concentration of ammonia in the final solution was about 0.1 ppm $NH_3 \cdot N$ or a total of 36 nanomoles of NH_3in 5 ml. This solution was covered and stirred for three minutes and then 5 μl of 100 ppm $NH_3 \cdot N$ (36 nanomoles NH_3) and 0.5 ml of 2.5N NaOH were added. The potential was measured at the plateau for five 5 μl incremental additions of 100 ppm $NH_3 \cdot N$ as described previously in the determination of slope. The original concentration of ammonia in the conditioning solution was determined by the Gran-plot of the measured potential versus the concentration of ammonia added in it. The analysis of actual samples was performed in a similar manner, as follows:

First, 2.0 ml of the conditioning solution followed by 10 µl of 1.0N HCl were added in the titration vessel and the obtained solution was stirred for three minutes. Second, 3.0 ml of the sample was added; the solution was stirred for at least two minutes to reach thermal equilibrium (25°C) and the electrode potential was measured after incremental addition of 5 µl of 100 ppm $NH_3 \cdot N$. The same technique as described for slope determination was used to obtain electrode potential. It is very important that the potential reading for any one addition of ammonia be taken at the potential vs time plateaus or when the change in potential for a one minute time interval is less than ± 0.5 mV. The concentration of ammonia in the sample was determined by subtracting the ammonia concentration of the conditioning solution (determined previously) from the total concentration of ammonia obtained from the Gran-plot.

RESULTS AND DISCUSSION

Accurate determination of the electrode potential and use of the correct slope of the electrode response with respect to concentration are the two most important factors of the Gran-plot technique. Accurate determination of the electrode potential is accomplished by utilizing the combination of electrometer (pH meter) and amplifier, described in the experimental part of this paper. With this, the electrode potential can be determined with an accuracy better than 0.2 mV which corresponds to a relative percent accuracy of better than 0.5%. The slope of the electrode response, theoretically, should be given by RT/nF, where R is the gas constant, T is the absolute temperature, n the number of the electrons, and F is the Faraday constant. In most cases the calculated (from the expression RT/nF) and the experimental values of the slope are so close that either one can be used in electrochemical calculations such as the Gran-plot technique. However, in the case of the ammonia electrode used in this study (Orion M-95-10), the experimentally determined slope was found to be considerably different (usually lower) from the theoretically calculated value. The average slope (E_m vs log $[NH_3]$) of twenty independent experiments conducted at 25°C over a period of ten days was found to be equal to 55 mV with a relative standard deviation of 2.3%. The range of the above slope value was 52.0 to 57.3 mV which is indicative of the day-to-day variation.

Figure 1 shows the effect of the slope value on the Gran-plot of one experimental run. The slope of the electrode response was experimentally determined to be 55 mV which, when it is used in the Gran-plot, results in an intercept equivalent to 32 nanomoles of ammonia. If, however, in the same run, another slope were used for the application of the Gran-plot technique, the resulting intercept would be substantially different. As shown in Figure 1, the intercept of the Gran plot for an electrode slope equal to 52 mV is equivalent to 21 nanomoles and the one corresponding to the theoretical value of 59 mV is equivalent to 46 nanomoles. This clearly demonstrates that an error of 100 to 200% may result from the use of an erroneous value of electrode slope. For this reason the slope of the electrode response should be determined separately before and after the application of

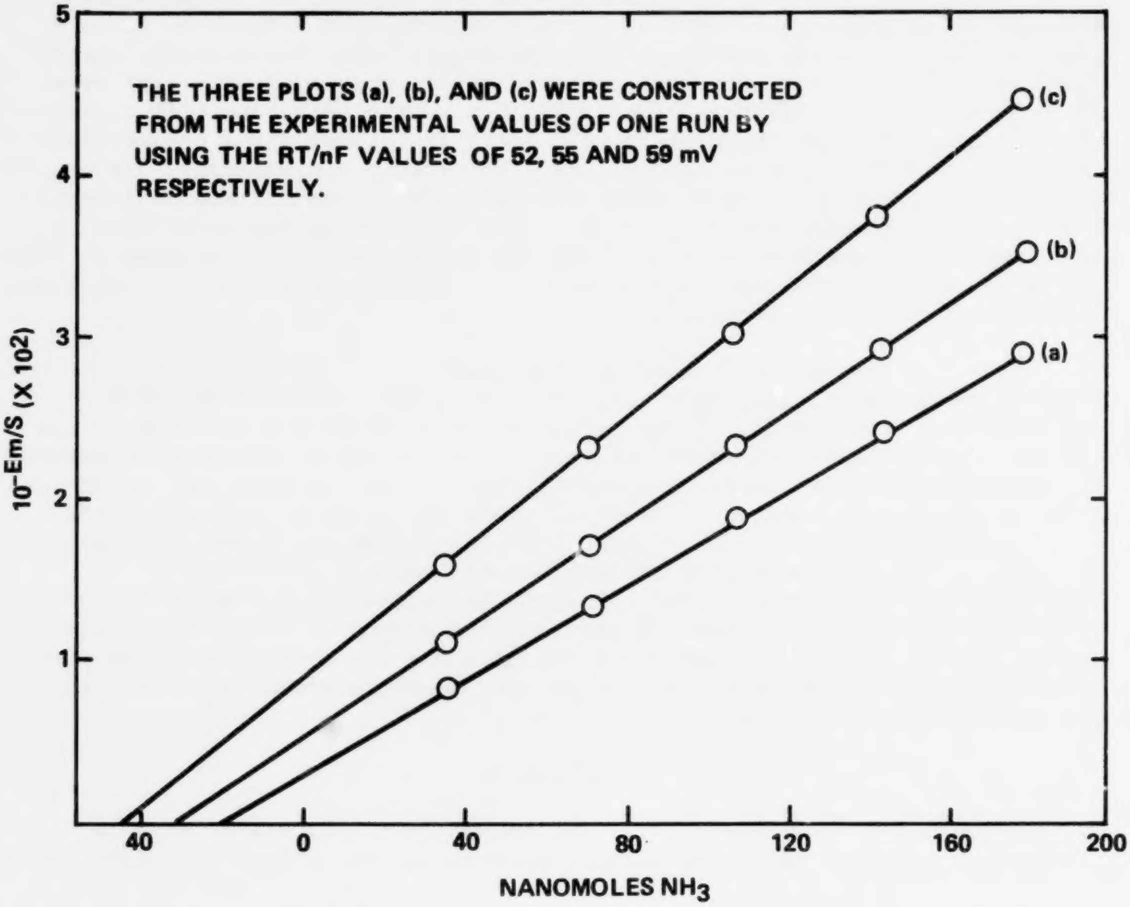

Figure 1. Effect of the RT/nF value (slope) on the intercept of the Gran-plot.

the Gran-plot technique in the determination of ammonia by an ammonia sensitive electrode. It should be noted here that the ratio Em/S is dimensionless and, therefore, the units in which the numerator and denominator of the ratio are expressed, are unimportant as long as they are the same. If, however, the theoretical value of the slope (mV) of the electrode response is used, the measured potential (Em) should be expressed in mV rather than in arbitrary units. This can be accomplished by calibrating the instrument against a standard voltage source.

During the development of this method, it was observed that analysis of synthetic solution containing ammonia in the range of 16-36 nanomoles produced fairly precise results (3-4% relative standard deviation) but not accurate (more than 12% error). Since the results were consistently lower than the expected value, it was hypothesized that losses of NH_3 *(gas) from the solution may be the cause of this problem. This hypothesis was corroborated by the fact that the difference between the expected and the obtained value was greater at low concentrations. To test this hypothesis, the use of conditioning solution was employed. This solution contained enough ammonia to bring the concentration up to a level not affected by the small loss which may take place during the performance of the analytical procedure. The use of conditioning solution appeared to eliminate the problem and, therefore, it was adopted in this procedure.*

Table I gives the results of the application of this method in the analysis of synthetic samples. From this it appears that the method produces accurate results for concentration above 16 nanomoles per 3 ml of the sample. To further demonstrate the validity of the developed method, samples of aqueous extracts of particulates collected at the sites of the Los Angeles Catalyst Study were analyzed. Table II shows the results obtained by the electrode method in relation to those obtained by the automated indophenol procedure. The good agreement between the two methods shows them to be equivalent and, therefore, application of this technique to the determination of ammonia in aqueous extracts of particulates should be acceptable. Currently, the described procedure is being used for the determination of particulate ammonium collected by the dichotomous samplers operating at the Los Angeles Catalyst Study sites.

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TABLE I. DETERMINATION OF AMMONIA IN SYNTHETIC SOLUTIONS BY THE GRAN-PLOT TECHNIQUE

Nanomoles NH_3		
	Found	
Taken	Average	Standard Deviation
8.04	6.7 (a)	± 2.4
16.1	16.0 (b)	± 0.6
20.7	20.7 (d)	± 2.1
33.2	33.2 (c)	± 1.1
61.7	58.7 (d)	± 1.0

(a) Average of eight determinations
(b) Average of six determinations
(c) Average of nine determinations
(d) Average of three determinations

TABLE II. DETERMINATION OF AMMONIUM IN AQUEOUS EXTRACTS OF PARTICULATES

	ppm NH_3		
Sample #	Ammonia Electrode	Automated Indophenol Method	% Diff.
1	8.37	8.86	- 5.7
2	5.09	4.99	+ 2.0
3	7.65	7.55	+ 1.3
4	5.09	5.25	- 3.1
5	5.23	5.05	+ 3.5
6	5.96	6.50	- 8.7
7	15.96	12.56	+11.9
8	41.52	41.68	- 0.4
9	41.12	42.75	- 2.0

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A COMPARISON OF THE THORIN AND MODIFIED METHYLTHYMOL BLUE METHOD FOR THE DETERMINATION OF MICRO-AMOUNTS OF SULFATE

George Colovos, Edward P. Parry, Allen M. Miles, and Martha R. Panesar

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The method developed by Brosset (Thorin method) for the microdetermination of sulfate is discussed and compared with the modified Methylthymol Blue method. Improvements made to the original Thorin method which increase the sensitivity, are discussed and the disadvantages presented. The sensitivity of the Thorin method has been increased without addition of sulfate (Brosset) to the reagents by increasing the excess of the Thorin reagent. The decrease of stability with time, the cost per sample and the reliability of measurement are the disadvantages of the method. The sensitivity of the conventional Methylthymol Blue method has also been increased by modifying the flow process so that no dilution of the sample occurs. Comparison of the sensitivity, precision and accuracy of the Thorin and modified Methylthymol Blue methods is made for the analysis of both synthetic and ambient samples.

INTRODUCTION

The property of thorin (o-[(2-hydoxy-3,6-disulfo-1-naphthyl)azo] benzenearsenic acid) which forms weak complexes with barium ions has been utilized in the determination of sulfate. J.S. Fritz and S.S. Yamamura (1) adapted first the use of thorin as indicator in the titrimetric determination of sulfate. They suggested use of an 80% ethanol-water mixture as the titration medium and $5 \times 10^{-3}M\ Ba(ClO_4)_2$ *as titrant. The sensitivity of this analysis was 10* $\mu g/ml\ SO_4^=$ *in a total volume of 25 ml. The sensitivity has been further studied and improved by other investigators. For instance, O. Menis, D.L. Manning, and R.G. Ball (2) replaced the 80% ethanolic titration medium with 50% isoamyl alcohol-water mixture and they also introduced a spectrophotometric method for the detection of the end-point.*

G. Persson (3) first developed a direct spectrophotometric determination of sulfate utilizing the barium-thorin complex. The reaction of sulfate with

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this complex results in formation of insoluble barium sulfate and release of free thorin. The extent of this reaction can be monitored spectrophotometrically at 520 nm, where the molar absorptivity of the barium-thorin complex is much higher than that of the free thorin. The decrease of the absorbence at 520 nm is, therefore, a measure of the amount of sulfate present in the sample. Persson automated this method and applied it to the determination of sulfur dioxide in air after absorption in a dilute solution of hydrogen peroxide.

Most recently, C. Brosset and M. Ferm (4) modified Persson's method and applied this modified version to the analysis of water soluble sulfate of airborne particulates. This version of the thorin method employs use of automatic repipets which allow rapid analysis of aqueous sulfate without the use of an autoanalyzer. This latter method has been utilized by us for the analysis of sulfate in suspended particulate samples collected by means of a dichotomous sampler. In the course of adopting this method of analysis, we investigated, to some extent, the chemistry involved and we also compared this against the methylthymol blue method (MTB), which is used routinely in our laboratory for the analysis of similar samples. In this paper the results of these studies are reported and discussed.

EXPERIMENTAL

INSTRUMENTS AND APPARATUS

A Perkin-Elmer Model 202 Ultraviolet-Visible spectrophotometer was used throughout these studies. This instrument has a double beam design with a photometric accuracy of 1% in the range of 0.0 - 1.0 absorbence units. The peak-to-peak noise of the instrument is not more than ± 0.005A at 1.0 absorbence unit. The photometric cells were Coleman spectrosil cylindrical cuvets with a transmission match of 1.5% at 240 mm. The cells had an internal light path of 20mm. For this particular analysis the spectrophotometer was adjusted as follows:

Both spectrophotometric cells were filled with reference solution (see below), then placed in the spectrophotometer and the instruments were adjusted to read zero at 520 nm. It is essential that the spectrophotometer be zeroed in this manner before any absorbence measurement for standards or samples are made. All spectrophotometric measurements were made against this reference.

The dispensing of samples dictated the need for specialized equipment that would be both semi-automatic and precise. Hence, the apparatus shown in Figure 1 was constructed. This apparatus consists of two piston operating pipets arranged in a way that precise mixing of an aliquot of the sample with the barium reagent can be achieved. For this, the tip of the double pipet is first submerged in the sample solution. Then the stopcock is opened and 2.0 ml of the sample is drawn into the sample loop using syringe A. The stopcock is closed and 5 ml of the barium-p-dioxane solution is drawn into syringe B which is then delivered via the sample loop into a mixing vessel. Finally, the stopcock is opened and the liquid of syringe A is also expelled into the mixing vessel.

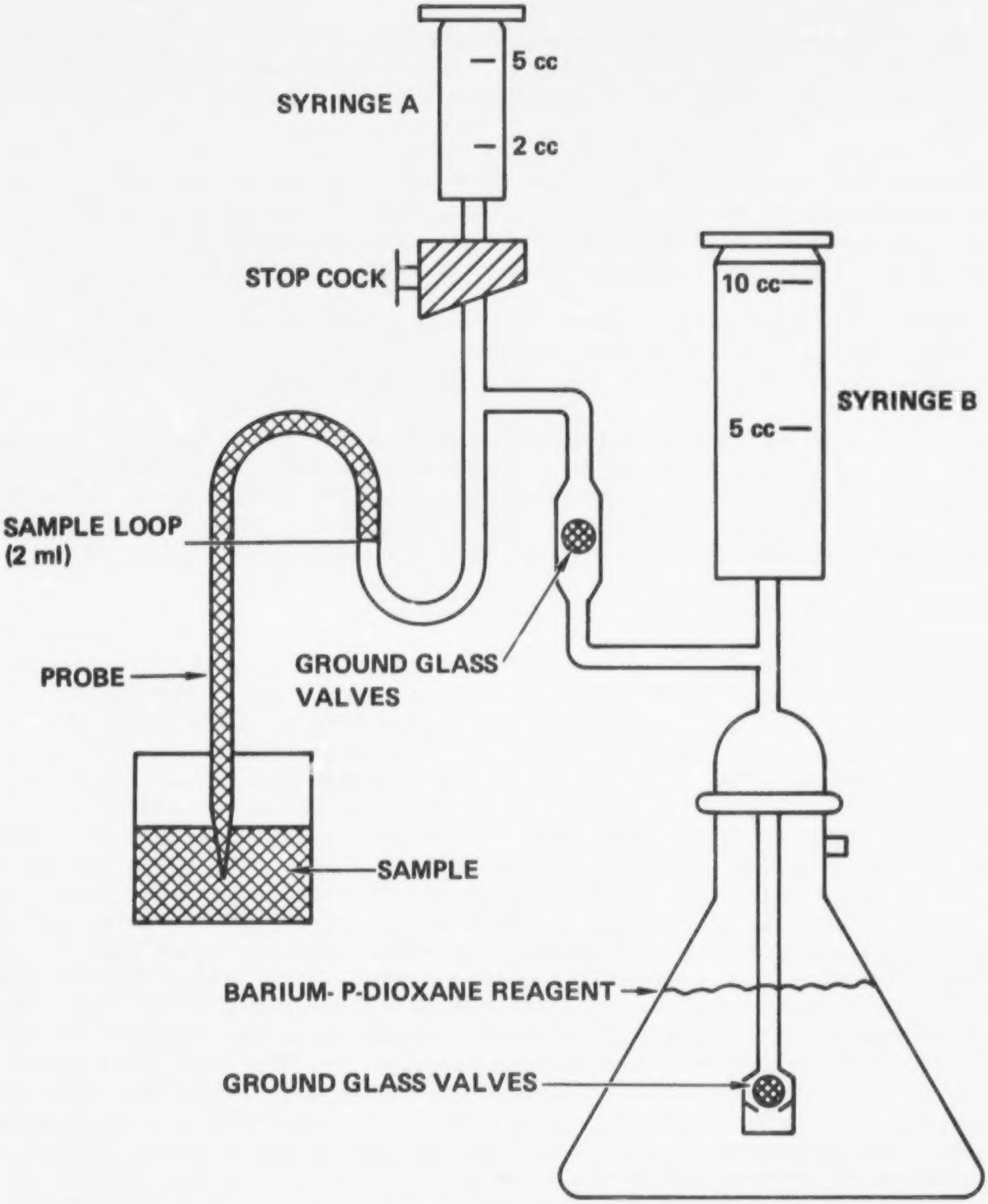
SYRINGE A
5 cc
2 cc
STOP COCK
10 cc
SYRINGE B
5 cc
SAMPLE LOOP
(2 ml)
PROBE
GROUND GLASS
VALVES
SAMPLE
BARIUM- P-DIOXANE REAGENT
GROUND GLASS VALVES

Figure 1. Double repipet used for mixing the sample with barium-p-dioxane reagent.

REAGENTS

All the chemicals used for the preparation of the necessary solutions were Baker analyzed reagent grade chemicals unless otherwise specified.

Barium stock solution was prepared by dissolving 525 mg of barium perchlorate dihydrate in 250 ml of 0.1N $HClO_4$. Barium-p-dioxane solution was prepared by diluting 5.0 ml of the stock barium perchlorate solution to 500 ml with p-dioxane.

Thorin dye solution was prepared by dissolving 250 mg of thorin in a beaker containing 10 ml 0.01N $NClO_4$. After dissolution of the dye was completed, the contents of the beaker were transferred quantitatively to a 100 ml volumetric flask and diluted to the mark with 0.01N $HClO_4$.

The ion-exchange resin (Dowex 50W-X8) used to remove the interfering cation must be in a fully swollen condition. This condition was achieved by soaking the resin in distilled water and drying by suction.

Sulfate standard solution was prepared by appropriate dilution of standardized sulfuric acid solution to a final concentration of 0.005N. This solution is equivalent to a $SO_4^=$ concentration of 240 ppm. It was used for the preparation of the standards in the thorin procedure. Usually the concentration of the standards used was in the range of 0.5 to 10 ppm.

PROCEDURE

A 10 ml aliquot of the sample solution to be analyzed was transferred into a 15 ml centrifuge tube containing 1 gram of the Dowex 50W-8X ion-exchange resin. The sample solution was then shaken with the resin for one hour. The samples were centrifuged for five minutes at 3000 rpm and 2.0 ml of the supernatant solution of each sample was pipetted into 25 ml volumetric flasks. After this, 5.0 ml of barium-p-dioxane solution was added into the volumetric flasks and the flasks were capped to prevent excessive evaporation of the p-dioxane. The pipetting and the mixing of the sample and barium-p-dioxane solutions were performed with the aid of the double pipet mentioned previously. Finally, an aliquot of 0.100 ml of the thorin solution, precisely measured with the aid of a micropipet, was added into the volumetric flasks. The resulting solutions were shaken well and then, after allowing time (three seconds) for bubbles to clear, the absorbence was measured at 520 nm. Absorbence measurements were made within three minutes after the addition of the thorin solution to sample. Blanks were prepared by using distilled water instead of standard solutions. Standard solutions and blanks were carried through all the steps of the analytical procedure simultaneously with actual samples. The reference solution was prepared by pipetting 4.0 ml of the distilled water supernatant used in the preparation of blanks, 10.0 ml of blank-p-dioxane (no barium) solution, and 0.200 ml of the thorin solution into a 25 ml volumetric flask. The resulting solution was shaken well. This reference is stable for more than eight hours.

RESULTS AND DISCUSSION

Early studies (3,4) have shown that the spectrophotometric method of analysis of sulfate by thorin was insensitive and inaccurate in the low concentration range (0 - 2.0 μg/ml $SO_4^{=}$). This was found to be the result of a substantial negative deviation of the response of the method to low concentrations of sulfate. This lack of response at the low concentration range was explained by Brosset, et al., by assuming incomplete precipitation of barium sulfate at this concentration range. To compensate for this, they added sufficient amounts of sulfate to the thorin reagent solution thus eliminating this problem. our studies have shown, however, that the same result can be brought about by changing the thorin-to-barium ratio. Figure 2 shows a typical calibration curve obtained by using our approach. The linearity of this curve is excellent (correlation coefficient 0.9999). To further show the consistency of this approach, the lower part of the calibration curve was studied separately. Figure 3 shows this part of the curve which was studied in increments of 1 μg sulfate (equivalent to 0.5 μg/ml in the extract). Even this part of the curve shows an extremely high linearity (correlation coefficient 0.998) and, therefore, the reason for the non-linear response obtained by Brosset, et al. can be attributed to incomplete complexation of the barium by thorin which results in relatively large concentrations of free barium ions in the solution. It is obvious that if free barium ions are present the sulfate will not react stoichiometrically with the barium-thorin complex, thus causing deviation from linearity. Figure 4 demonstrates the formation of the barium-thorin complex. In this, the absorbence of solutions containing constant concentration of thorin and variable concentrations of barium ions was measured at 520 nm against a reference solution containing identical concentrations of thorin. Therefore, the increase in absorbence represents the formation of the barium-thorin complex, and the plateau shows the completion of this reaction. The thorin-to-barium molar ratio at the intercept of the rising and horizontal lines is 1.9:1 which indicates the formation of 1:2 barium-to-thorin complex. Since the absorbence reading is a measure of the formation of the complex, the difference between the observed and the anticipated absorbence (intercept of the two lines) at the equivalence point should be a measure of the degree of dissocation of the complex. Therefore, this difference can also be utilized for the estimation of the concentration of free barium ions at the equivalence point. If A_{max} is the maximum absorbence obtained with excess of barium and A_{equiv} the observed at the equivalence point, the concentration of the free barium ($[Ba^{++}]_{free}$) at the equivalence point will be

$$[Ba^{++}]_{free} = [Ba^{++}]_{equiv} = \frac{A_{equiv}}{A_{max}} [Ba(th)_2]_{max} \tag{1}$$

and since $[Ba(th)_2]_{max} = [Ba^{++}]_{equiv}$

$$[Ba^{++}]_{free} = \frac{A_{max} - A_{equiv}}{A_{max}} [Ba^{++}]_{equiv} \tag{2}$$

where $[Ba(th)_2]_{max}$ and $[Ba^{++}]_{equiv}$ are the maximum concentration of the barium-thorin complex and the total concentration of barium at the equivalence point, respectively.

In the experiment of Figure 4, A_{max} and A_{equiv} are 0.775 and 0.700, respectively, and therefore,

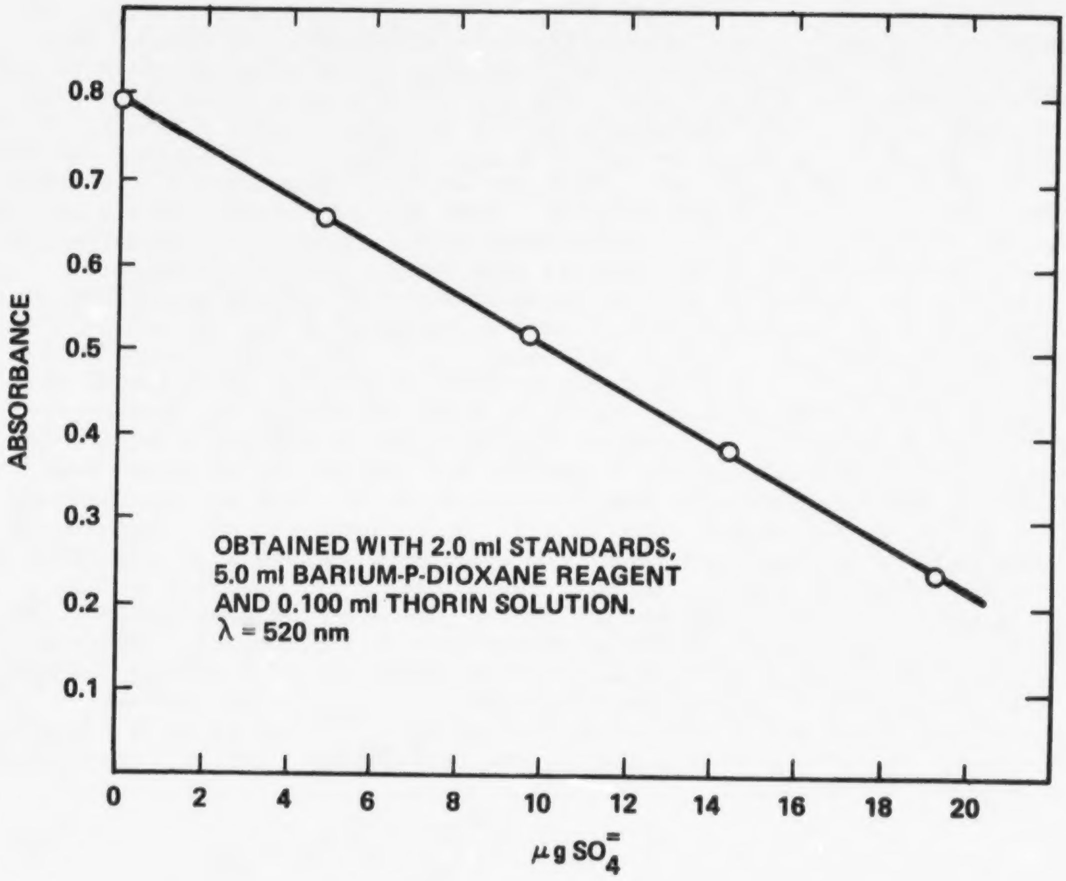

Figure 2. Calibration curve for the range 0-20 μg $SO_4^=$.

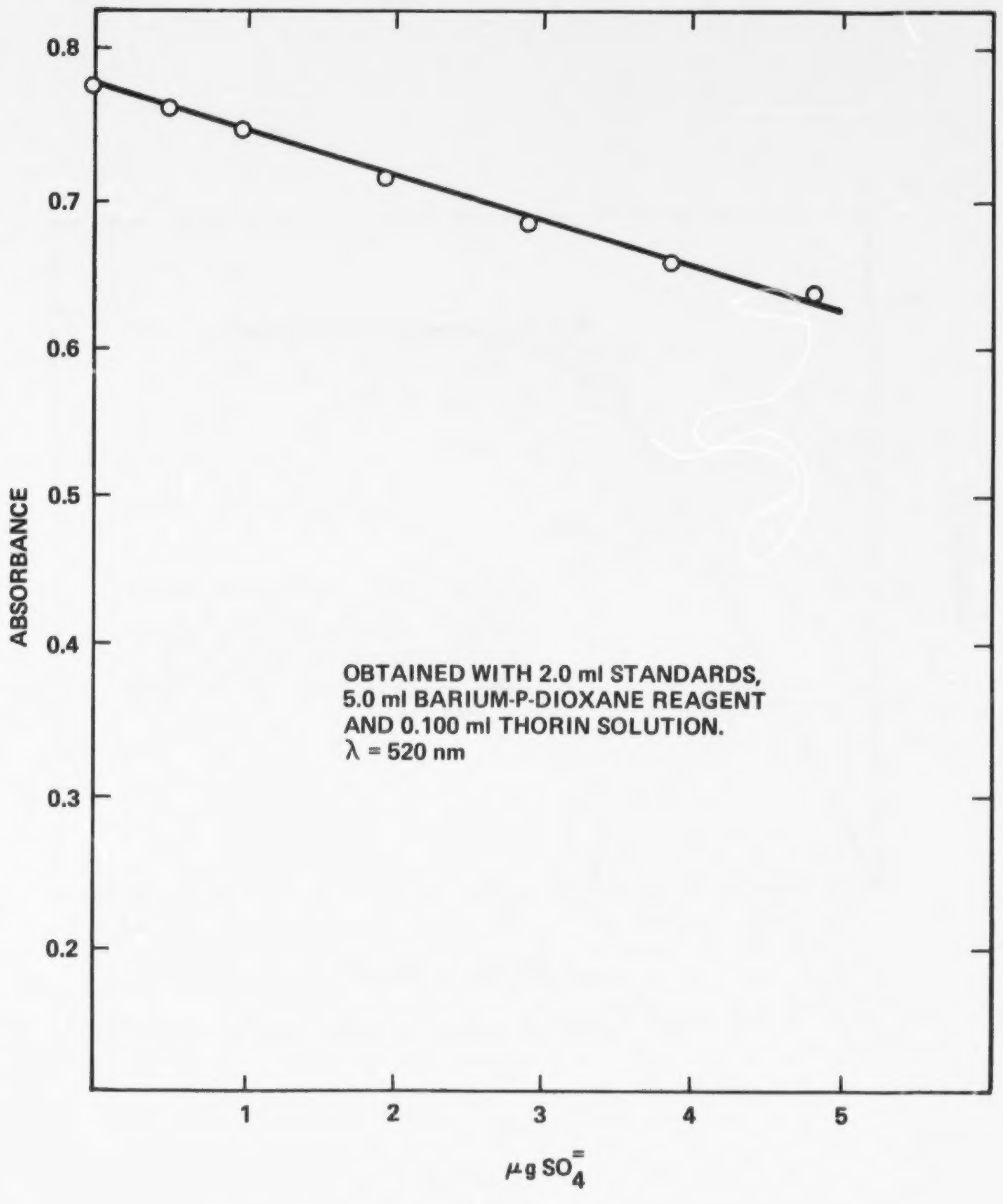

Figure 3. Calibration curve for the range 0-5 μg $SO_4^=$.

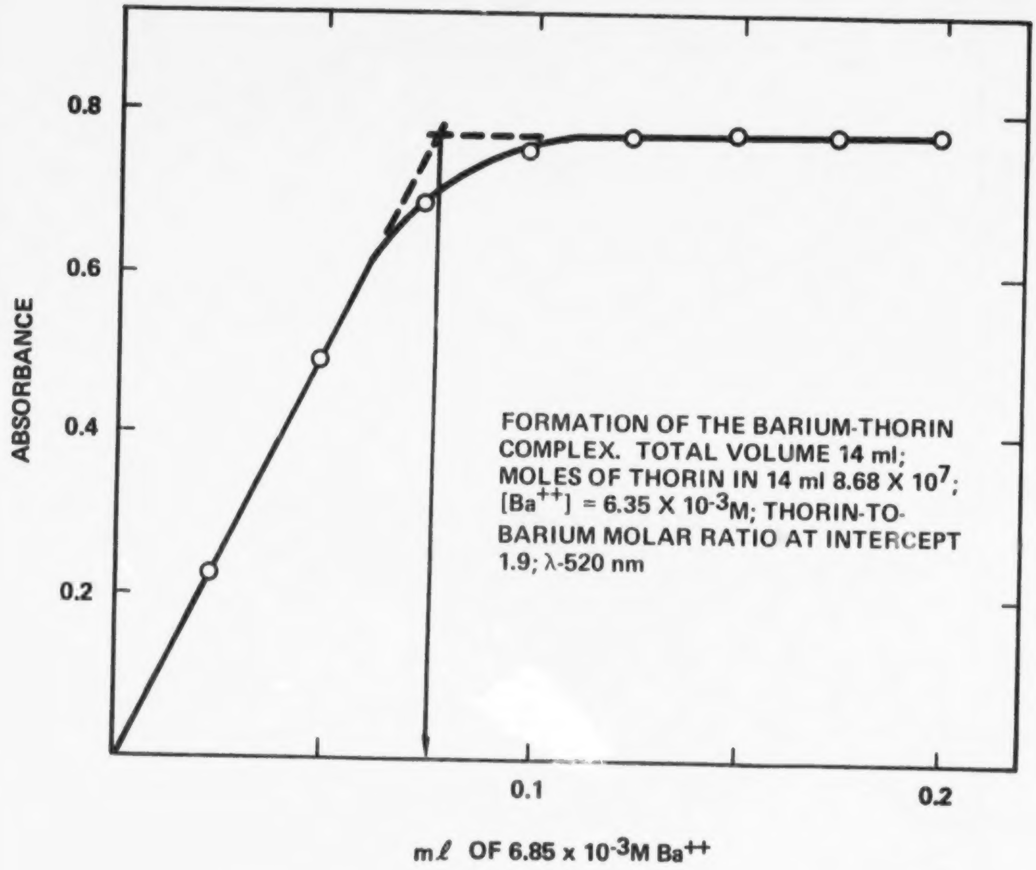

Figure 4. Spectrophotometric demonstration.

$$[Ba^{++}]_{free} = 0.107\ [Ba^{++}]_{equiv.}$$

Therefore, almost 11% of the barium at the equivalence point remains uncomplexed and it would cause non-linear response for low concentrations of sulfate. Obviously this can be avoided by adding sufficient excess of thorin which will complex all the available barium. As was mentioned previously, this approach did eliminate the non-linearity problem yielding calibration curves consistently similar to those presented in Figures 2 and 3, provided that the absorbence reading of each solution was taken within three minutes after the addition of the thorin reagent. When the absorbence was measured differently, the obtained results were not as precise as those shown in Figures 2 and 3. This was found to be caused by a change in the absorbence of the sample solutions with time.

Figure 5 presents absorption spectra of barium-thorin (1:2) and plain thorin solutions taken at 0, 10, 20, 30 and 40 minutes after their preparation. During this period of time, the spectrum of the plain thorin solution remained unchanged but that of the solution containing the complex showed a significant decrease in absorbence. The decrease in the absorbence of the solution containing the complex can be attributed to either catalytic decomposition of the free thorin existing in solution or precipitation (or decomposition) of the barium-thorin complex. It is rather evident that the decrease in the concentration of the free thorin and barium-thorin species in a solution can be estimated as follows by measuring its absorbence at two different wavelenghts. If $\varepsilon_{(th)_1}$, $\varepsilon_{[Ba(th)_2]_1}$ *and* $\varepsilon_{(th)_2}$, $\varepsilon_{[Ba(th)_2]_2}$ *are the molar absorptivities of the free thorin and the barium-thorin complex at wavelengths* λ_1 *and* λ_2*, respectively, then the absorbence of these two wavelengths should be given by equations (4) and (5) below*

$$A_1 = \varepsilon_{(th)_1} C_{(th)} + \varepsilon_{[Ba(th)_2]_1} C_{[Ba(th)_2]} \qquad (4)$$

$$A_2 = \varepsilon_{(th)_2} C_{(th)} + \varepsilon_{[Ba(th)_2]_2} C_{[Ba(th)_2]} \qquad (5)$$

where $C_{(th)}$ *and* $C_{[Ba(th)_2]}$ *are the concentrations of the free thorin and of the barium-thorin complex, respectively.*

The concentrations of the two species can then be estimated from the absorbence values obtained at the two wavelengths, provided that the molar absorptivities $\varepsilon_{(th)_1}$, $\varepsilon_{(th)_2}$, $\varepsilon_{[Ba(th)_2]_1}$ *and* $\varepsilon_{[Ba(th)_2]_2}$ *are known. The values of the molar absorptivities of these two species can be estimated independently by measuring the absorbences of solutions containing known concentrations of plain thorin and of barium-thorin complex at the two wavelengths* λ_1 *and* λ_2*.*

Figure 6 presents graphically this type of estimation for an experimental set similar to the one described previously in Figure 5. From this, it can be calculated that the decrease of free thorin concentration during the 60 minute period, accounts only for 7.7% of the total decrease in concentration, whereas the change in the concentration of the complex accounts for the rest.

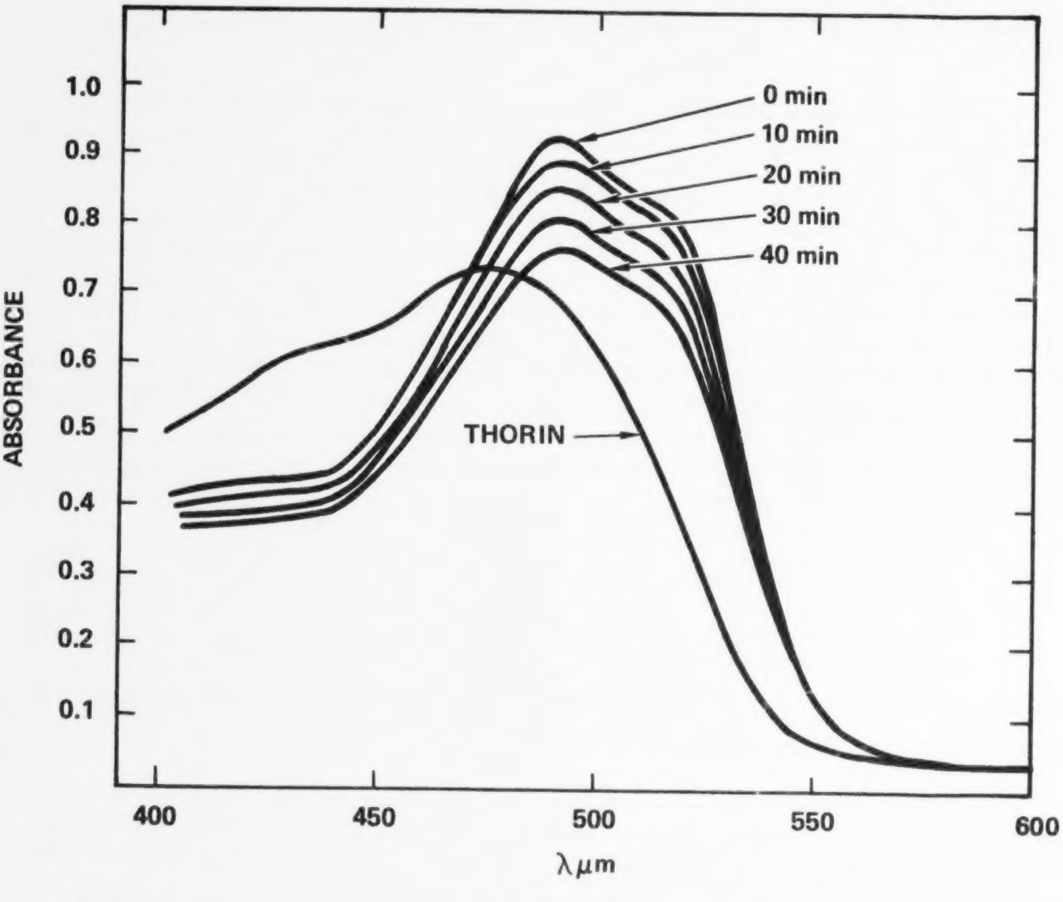

Figure 5. Spectral change of the barium-thorin complex with time.

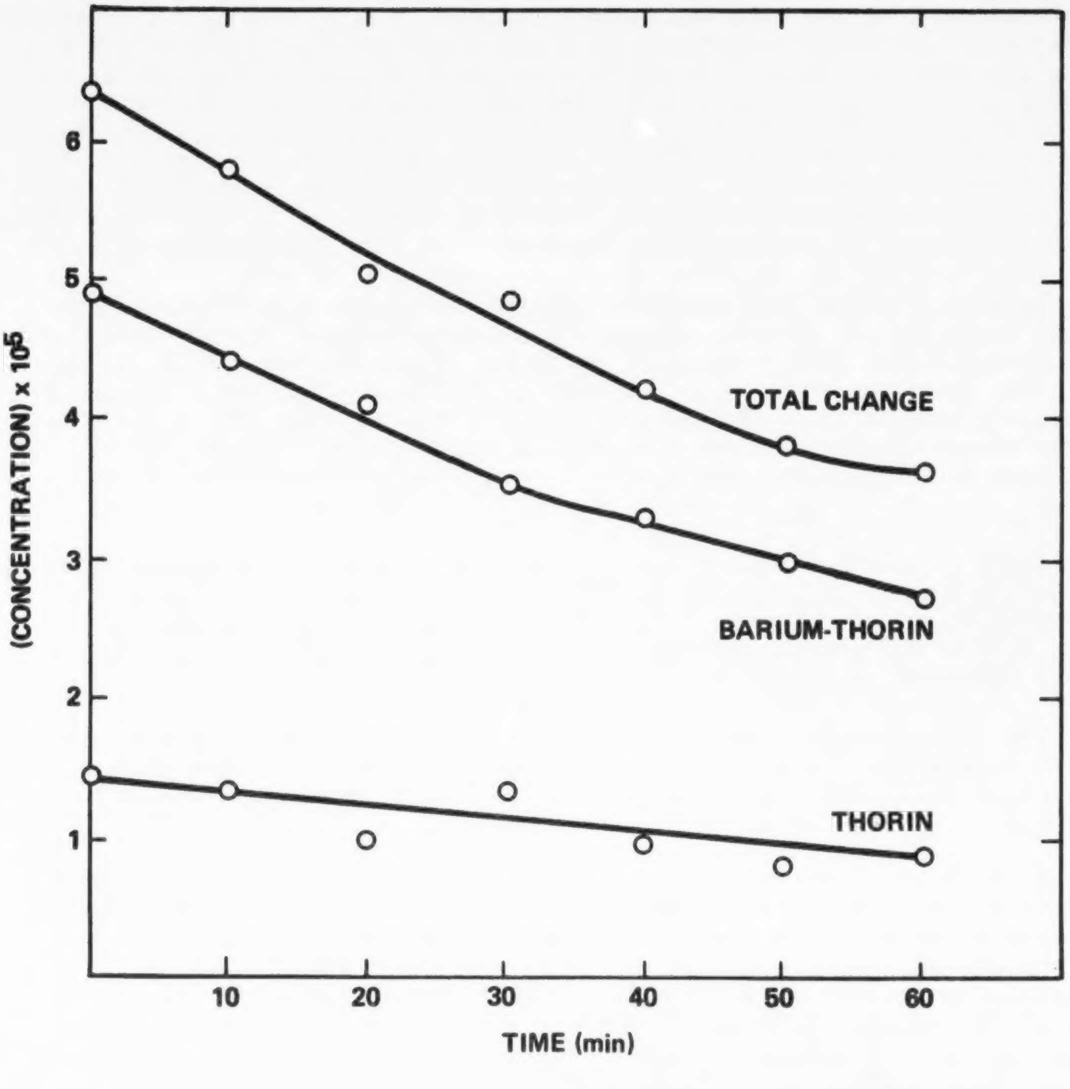

Figure 6. Rate of decrease of concentration of the thorin and barium-thorin species from solution.

This indicates strongly that this reaction proceeds via a mechanism of precipitation of the barium-thorin complex. This indication is corroborated by the fact that a substance of similar color with that of the complex precipitates out when solutions containing the complex are left overnight. Formation of the same reddish precipitate was also observed in the automated thorin procedure developed by Persson (3). Because of this kinetic phenomenon, the measurement of the absorbence should be made as soon as possible after the addition of the thorin reagent and it should never be delayed for more than three minutes. It should also be mentioned here that during these studies a substantial increase in stability occurs when about three-fold excess of thorin is used. Thus, we adopted the procedure in which the barium-to-thorin ratio is 1:3. This assures complexation of all the available barium and it also increases the stability of the samples. The results of the application of this procedure to the analysis of synthetic samples, as well as comparison against the modified methylthymol blue method (5) will be presented below.

Table I presents precision data obtained by analyzing multiple samples at two concentration levels. The relative standard deviation for the low and high concentration levels was found to be 5.2% and 1.6%, respectively. The decreased precision at the low level can be attributed to a small change of absorbence between the blank and the sample. Also the rate of precipitation of the barium complex may have a role in this since the concentration of that complex is considerably higher at the low concentration than at the higher.

Table II presents results for the analysis of high-volume sample extracts by the thorin and the automated methylthymol blue methods. Because of the relatively high concentration of sulfate in these extracts, the samples had to be diluted for the thorin procedure. The relative difference of the two values was found to be in the range of 0.5 to 15%.

Table III shows data obtained from the analysis of aqueous extracts of four-hour membrane filter samples. Although the correlation data shown in this table indicate a bias of about 10%, the overall agreement appears to be good especially for the higher concentrations.

In Table IV, x-ray fluorescence sulfur data obtained from the analysis of dichotomous samples are compared with those obtained by the thorin method. The 1000 series filter numbers correspond to the sample of fine particles and the 3000 series to the total particles. As it is shown in Table IV, better agreement was obtained in the analysis of the fine particles than in that of the totals. This may be the result of particle size effect in the x-ray fluorescence analysis of the total samples. Despite these differences, the agreement appears to be fairly good.

All these analytical data have shown clearly that the thorin method generates fairly accurate results when it is used properly. However, a close comparison of this method with the modified methylthymol blue procedure (5) revealed the following advantages of the latter over the thorin procedure: (1) the cost per analysis is significantly lower for the automated methylthymol blue method; (2) the manpower required is lower by a factor of five; and (3) the expense for chemicals is minimal if it is compared with the cost of

TABLE I. REPEATED ANALYSES OF SYNTHETIC SULFATE SOLUTIONS BY THE THORIN METHOD

	(μg $SO_4^=$)	
Present	Found	% Diff.
4.8	4.99	3.96
4.8	5.03	4.79
4.8	4.75	-1.04
4.8	4.43	-5.63
4.8	4.64	-3.33
9.60	9.62	0.2
9.60	9.66	0.6
9.60	9.52	-0.8
9.60	9.48	-1.3
9.60	9.66	0.6
9.60	9.60	0.0
9.60	9.30	-3.1
9.60	9.80	2.1
9.60	9.70	1.0
9.60	9.79	1.9

TABLE II. RESULTS OF SULFATE ANALYSIS OF HIGH-VOLUME SAMPLES BY BOTH THE THORIN AND THE AUTOMATED METHYLTHYMOL BLUE METHOD

Sample No.	μg/ml		
	Thorin	Technicon	% Diff. *
63191	32.13	31.3	+ 2.6
63192	29.37	30.9	- 5.0
63193	18.50	16.1	+13.8
63194	19.63	17.0	+14.4
63195	12.88	14.0	- 8.4
63196	16.69	16.8	- 0.6
63195	14.26	13.7	+ 4.0
63292	27.51	29.7	- 9.6
63293	19.75	19.8	- 0.3
63294	18.79	17.6	+ 6.6
23393	16.10	18.8	-15.4
23394	17.80	19.8	-10.6
23395	10.90	11.8	- 7.8
12478	35.23	34.1	+ 3.2
12481	35.78	31.8	+11.8
12484	18.13	17.9	+ 1.3

$$* \pm \% \text{ Diff.} = \frac{\Delta[SO_4^{=}]}{[SO_4^{=}]_{aver.}} \times 100$$

TABLE III. COMPARISON OF SULFATE VALUES OBTAINED BY THE MTB (RANGE 1-10) & THORIN (BROSSET) METHODS FOR 4-HOUR MEMBRANE FILTER SAMPLES

(LACS SITE A 15-19)

Sampling Date	$SO_4^=$ µg/m^3 MTB	$SO_4^=$ µg/m^3 Thorin
125	9.56	11.93
130	7.17	6.41
133	10.07	12.40
136	11.03	10.89
139	5.50	7.30
142	8.54	10.31
145	17.04	17.28
148	32.66	34.51
154	13.26	14.41
157	10.49	11.29
160	20.81	20.59

LINEAR LEAST SQUARES DATA:

Intercept	-1.13
Slope	-0.898
Standard Error	-1.03
Coefficient of Correlation	-0.99

TABLE IV. RESULTS OF SULFATE ANALYIS OF DICHOTOMOUS SAMPLES BY X-RAY FLUORESCENCE AND THORIN PROCEDURES

	$\mu g/m^3$ S		
Filter No.	XRF *	Thorin	% Diff.
1136	1.36	1.46	7.1
3136	1.34	1.66	21.3
1129	3.01	2.89	4.1
3129	1.57	2.29	37.3
1124	4.17	4.61	10.0
3124	3.20	4.01	22.5
1130	3.34	3.64	8.6
3130	2.00	2.19	9.1
		Average	15.0%

* Samples analyzed independently by Lawrence Berkeley Laboratory

chemicals used in the thorin method which in 1976 was approximately 70¢ per sample. In addition, but most important, the p-dioxane which is used in the thorin method is a health hazard and prolonged exposure can cause severe damage to humans. For these reasons, an additional effort was made to determine better the equivalency of the two methods.

To check the correlation between the two methods, actual particulate samples collected on 27 mm Teflon filters were analyzed. The filters were extracted according to established procedure and aliquots of the extract analyzed by both methods. The results given in Table V show the agreement between duplicate analyses on the same extract by the thorin method. As indicated in the column labeled "% Diff.", duplicate results may deviate from the average value by a maximum of ± 6.4%. Table VI shows the comparison between the average values from Table V and the values obtained by the MTB method. The correlation between the two methods is better than 95% (correlation coefficient 0.99), although a bias of about 9% between the two methods does exist. Finally, the two methods were compared in a determination of the background levels of sulfate (blank) in three different filtering media. For this, individual filters were extracted with water and each extract was analyzed by both methods. From Table VII it becomes apparent that the standard deviation of the thorin results is much higher than those of the methylthymol blue method. This can be attributed to the lower precision of the thorin procedure because the sensitivity of both methods is about the same.

From all these experiments it was concluded that either method can be used for the analysis of particulates collected by the dichotomous sampler. However, because of the above mentioned advantages, the automated methylthymol blue method was selected for the analysis of the Los Angeles Catalyst Study dichotomous samples which are also analyzed for total sulfur by x-ray fluorescence at the Lawrence Berkeley Laboratory at the University of California (6). Statistical analysis of the results obtained by wet chemistry (modified MTB) and x-ray fluorescence revealed good correlation between the two methods.

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TABLE V. DUPLICATE ANALYSIS OF SULFATE BY THE THORIN METHOD IN AQUEOUS EXTRACTS OF PARTICULATE COLLECTED ON 37 mm TEFLON FILTERS

Sample No.	$\mu g\ SO_4^-$		$\mu g\ SO_4^=$	
	1st Run	2nd Run	Average	%Diff.
1204	189.72	182.65	186.18	+ 3.8
3204	176.95	187.79	182.37	- 5.9
1205	134.81	145.61	140.21	- 7.7
3205	152.57	144.86	148.72	+ 5.2
1206	207.99	200.46	204.22	+ 3.7
3206	236.84	241.18	239.01	- 1.8
1207	227.01	257.87	242.44	-12.7
3207	243.36	244.40	243.88	- 0.4
1208	107.05	102.59	104.82	+ 4.3
3208	140.5	-	140.5	-
1209	223.75	213.79	218.77	+ 4.6
3209	229.53	243.33	236.43	- 5.8

TABLE VI. COMPARISON OF SULFATE DATA OBTAINED BY THE THORIN METHOD AND THE AUTOMATED METHYLTHYMOL BLUE METHODS

	$\mu g/SO_4^=$		
Sample No.	Thorin	MTB	% Diff.
1204	186.18	178.53	+ 4.2
3204	182.37	166.67	9.0
1205	140.21	135.37	+ 3.5
3205	148.72	149.82	- 0.7
1206	204.22	205.98	- 0.8
3206	238.01	227.54	+ 4.9
3207	243.88	228.80	+ 6.4
1208	104.82	101.60	+ 3.1
3208	140.5	127.86	+ 9.4
1209	218.77	197.55	+10.2
3209	236.43	219.30	+ 7.5

TABLE VII. DETERMINATION OF THE BACKGROUND SULFATE LEVELS (BLANK) IN THREE DIFFERENT FILTERING MEDIA BY THE THORIN AND THE SENSITIVE MTB METHODS

	Total µg $SO_4^=$ *			
	Thorin		MTB	
Type of Filter	Average	Standard Deviation	Average	Deviation
Gelman Acropore (120 mm)	45.76	9.38	43.42	4.15
Millipore Cellulose Ester (102 mm)	24.52	4.85	28.25	0.22
Fluoropore (37 mm)	0.476	0.15	0.388	0.05

* Average of independent analysis of five filters.

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X-RAY FLUORESCENCE ANALYSIS OF LACS AEROSOLS

R.D. Giauque, R.B. Garrett, and L.Y. Goda

Lawrence Berkeley Laboratory
Berkeley, California

G. Colovos and E. Parry

Rockwell International Air Monitoring Center
Newbury Park, California

C. Rodes and F. Burmann

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The concentrations of eight elements: sulfur, lead, bromine, chlorine, zinc, silicon, calcium, and iron in aerosol specimens collected during the Los Angeles Catalyst Study program, have routinely been determined by x-ray induced x-ray fluorescence analysis. Correlations among pairs of elements have been observed. Also, at the sites used for the study, maximum levels of particulate sulfur due to emissions from vehicles equipped with catalytic converters are estimated. Good agreements typically obtained between total sulfur from the method and wet chemical methylthymol blue sulfate data suggest that over 90% of the particulate sulfur is present as sulfate. The capabilities and limitations of the x-ray fluorescence technique, as it applies to analysis of aerosol specimens collected during this program, is discussed. Results from specific experiments are included.

INTRODUCTION

The analytical technique of x-ray fluorescence (XRF) lends itself to simultaneous nondestructive determination of a broad range of elements in aerosol specimens collected on filter media. The technique is quantitative and high sensitivities are obtainable ($\sim$30 ng/cm^2 using two minute counting periods).

During the Los Angeles Catalyst Study (LACS) program, the concentrations of eight elements were routinely ascertained for three types of specimens: total aerosols (4- and 24-hr); size segregated aerosols acquired with dichotomous samplers (24-hr); and Anderson cascade after filter specimens (24-hr) for which particles $<0.7\mu$ are collected.

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DISCUSSION OF METHOD

Figure 1 is a schematic diagram of the XRF system used for analysis of LACS aerosol specimens. Radiation provided by an x-ray tube impinges upon the filter media containing the collected particulate matter. A fraction of the photons, if of sufficient energy, produce vacancies in the inner shells of atoms within the specimens, and in turn characteristic x-rays are emitted. These x-rays are detected by a semiconductor detector, sorted by their energies, and the elemental concentrations are determined from the intensities of the x-rays.

In addition to the above interactions, a portion of the excitation radiation is scattered. For analyses of aerosols collected on filter media, the intensity of the scattered x-rays is often quite large in contrast to those of the characteristic x-rays. In order to obtain high intensities, near monochromatic excitation radiation with energies slightly greater than the K or L absorption edges of the elements to be analyzed is used.

EQUIPMENT

The x-ray system in the direct excitation mode is shown in Figure 1. It consists of a low power silver anode x-ray tube and transmission filters. The cryostat design allows the excitation radiation to pass through the vacuum cryostat, permitting minimum x-ray attenuation, as an air path of only 1.5-mm exists between the specimen and the detector window (0.002-cm beryllium). In the determination of low atomic number elements: silicon (Si), sulfur (S), chlorine (Cl), and calcium (Ca), the x-ray tube is operated at 9 KV and 200 μamps, and a 0.00025-cm silver filter is used. The x-ray tube is operated at 37 KV and 600 μamps, and a 0.007-cm silver filter preceded by a 0.025-cm vanadium filter are utilized for the determination of heavier atomic number elements: iron (Fe), zinc (Zn), bromine (Br), and lead (Pb).

Table I list the theoretical detection limits (presuming no overlapping x-rays) of the x-ray system for aerosol specimens collected on cellulose ester membrane filters. These detection limits are based on two 2-minute analysis periods. An air flow of 2.5 m^3/cm^2 (typical sampling rate for 24-hr membrane filters) is presumed.

CALIBRATION METHOD

STANDARDIZATION

To calibrate a spectrometer for analysis of air particulate specimens collected on filter media, it is necessary to determine the sensitivity of the system for each of the elements to be analyzed. The sensitivity, S, for an element i may be expressed:

$$S_i = I_i/m_i \qquad (1)$$

where S_i = the sensitivity in counts/sec per $\mu g/cm^2$;

I_i = The intensity, counts/sec, of the x-ray line from an elemental thin film (matrix effects presumed to be negligible); and

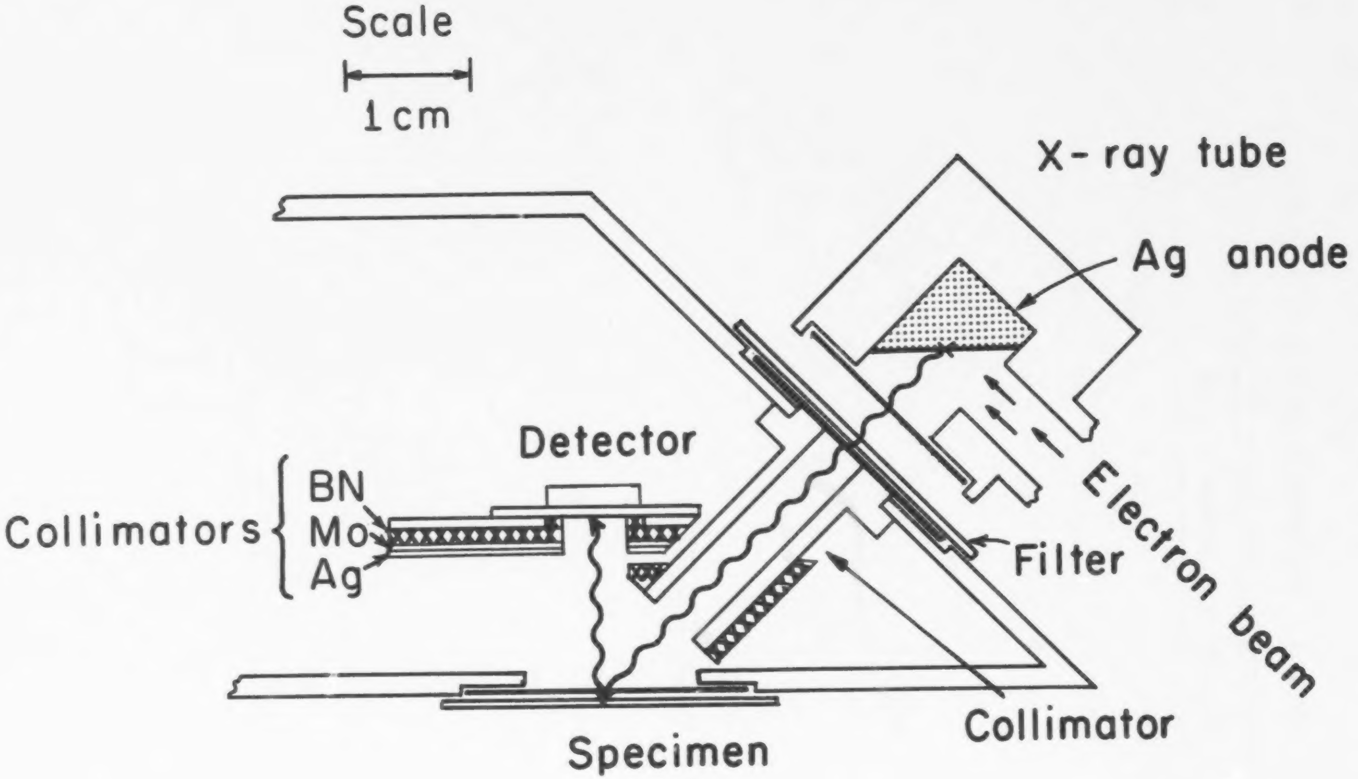
Scale
1 cm
X-ray tube
Ag anode
Detector
Collimators
BN
Mo
Ag
Electron beam
Filter
Collimator
Specimen

Figure 1. Schematic diagram of x-ray fluorescence system.

TABLE I. THEORETICAL DETECTION LIMITS

Element	Spectral Line	
Si	Kα	0.03 μg/m^3
S	Kα	0.02
Cl	Kα	0.03
Ca	Kα	0.06
Fe	Kα	0.09
Zn	Kα	0.03
Br	Kα	0.01
Pb	Kα	0.03

m_i = the mass of the elemental thin-film, $\mu g/cm^2$.

Relative excitation-detection efficiencies of the system for x-ray lines from Ca, Fe, Zn, Br, and Pb were determined utilizing multielement solution deposits on thin substrata (1). One of the elements, copper (Cu), in each multielement standard solution served as an internal standard. Actual standardization of the system was achieved using a single element thin-film standard which was prepared by vacuum vapor deposition of pure Cu onto a thin substrate.

Standardization for Cl was made with a basic physical approach (calculations using x-ray cross section and fluorescent yield data from the literature).

Thin film deposits of Si and S, for which matrix effects of low energy x-rays from the elements would be negligible, are difficult to prepare. Consequently, thick pure element discs of Si and S were used to standardize for analysis (1). The mass, m_{thick} ($\mu g/cm^2$), of a thick element disc is expressed:

$$m_{thick} = 3.92/(\mu_e \csc\Psi_1 + \mu_f \csc\Psi_2) \qquad (2)$$

where μ_e and μ_f = the total mass absorption coefficient of the element ($cm^2/\mu g$ for the excitation and fluorescent radiations, respectively; and Ψ_1 and Ψ_2 = the angles formed by the excitation and fluorescent radiations with the surface of the disc.

Since m_{thick} represents the mass of which only 25% of the radiation (excitation x fluorescent) is not attenuated, the mass of the disc for standardization purposes is 0.25 x m_{thick}.

Cross checks on standardization procedures are reported in detail elsewhere (1). Standardization for Ca, Fe, Zn, Br, and Pb are estimated to be accurate to within 1% or better, for Si and S to within 3% or better, and for Cl to within 5%.

DETERMINATION OF OVERLAPPING SPECTRAL PEAK CORRECTIONS

The analysis program uses a fixed number of channels to measure characteristic x-ray line intensities of each element to be determined. Peak overlaps were established from x-ray spectra generated from thin deposits of each element. S K and Pb M x-rays are the most critical overlap, as they are quite close in energy.

Small particles containing Pb from automotive emissions can collect as conglomerations on the filter. This has been observed with scanning electron microscope (SEM) photographs by Dr. Thomas Hayes of Lawrence Berkeley Laboratory. Additionally, large particles containing Pb (>1μ) are collected when sampling near the freeway. In each of the above two cases, particle size effects exist for Pb M x-rays. It was determined that using a direct relationship between high energy Pb L and low energy Pb M x-rays to predict the Pb M overlap with S K x-rays produced S results which were low due to an overcorrection; consequently, S K and Pb M x-rays are simultaneously unfolded for the S *analysis. Figure 2 illustrates this overlap for a 24-hour aerosol specimen. Listed in the figure are the element concentrations, μg/m^3, for this specimen (2.5 m^3 of air was sampled (cm^2).*

All other spectral peak overlaps were usually very minor, and, in most cases, the corrections amounted to a few percent or less.

Approximately 2.5 m^3 of air was sampled per 1 cm^2 of filter area for aerosol specimens collected over 24-hr periods. The amount of particulate Pb collected usually varied from 2 to 30 μg/cm^2. Consequently, a small fraction of the low energy x-rays from Si, S, and Cl are attenuated by the automotive particulate loading. Corrections were made in the analysis program for absorption effects due to these loadings. From the Pb concentration determined, using the higher energy Pb L α x-ray line (10.5 keV), absorption corrections are calculated on the assumption that these loadings are distributed uniformly across the filter and the composition of the Pb compounds in the particulate matter is PbBrCl. For S K x-rays the absorption correction was 3% for 5 μg, and 10% for 20 μg of Pb/cm^2. Absorption corrections applied for aerosol specimens collected over 4-hr periods, in nearly all cases, were 2% or less.

ABSORPTION CORRECTION FOR SULFUR DUE TO PENETRATION OF SULFUR PARTICLES INTO FILTER MEDIA

Giauque, et al., have reported (2) that attenuation of S K x-rays, due to penetration of the S containing particles into the filter media, is much less than 5%. This was based on experimental determinations of S using different energies of excitation radiation which acted as variable depth probes.

More recently, Loo et al., (3), have substantiated our conclusions by comparing XRF data for monodisperse $CuSO_4$ and K_2SO_4 aerosols collected on both cellulose ester membrane filters and on very small pore Nucleopore polycarbonate (surface collection media) filters.

In the XRF program used for the LACS program a 2% correction is made for the attenuation of S K x-rays due to particle penetration.

ABSORPTION CORRECTION DUE TO PARTICLE SIZE EFFECTS

The source of Si is usually wind-blown soil dust. Particles containing Si are usually greater than several microns. A sizeable fraction of the Si K x-rays (1.74 keV) are attenuated in sedimentary particles containing silicon. Initially, two dozen 24-hr membrane aerosol samples were analyzed using different energies of excitation radiation (Zr, L, Ag L, and Ni K x-rays), which served as variable depth probes to ascertain average particle size corrections to be applied for the Si analysis. The actual procedure used is reported elsewhere (2). These corrections for aerosol samples collected on membrane filters were typically around a factor of 2 (i.e., over half of the Si K x-rays are absorbed in the sedimentary particles).

For the S analysis, no corrections were made for particle size effects.

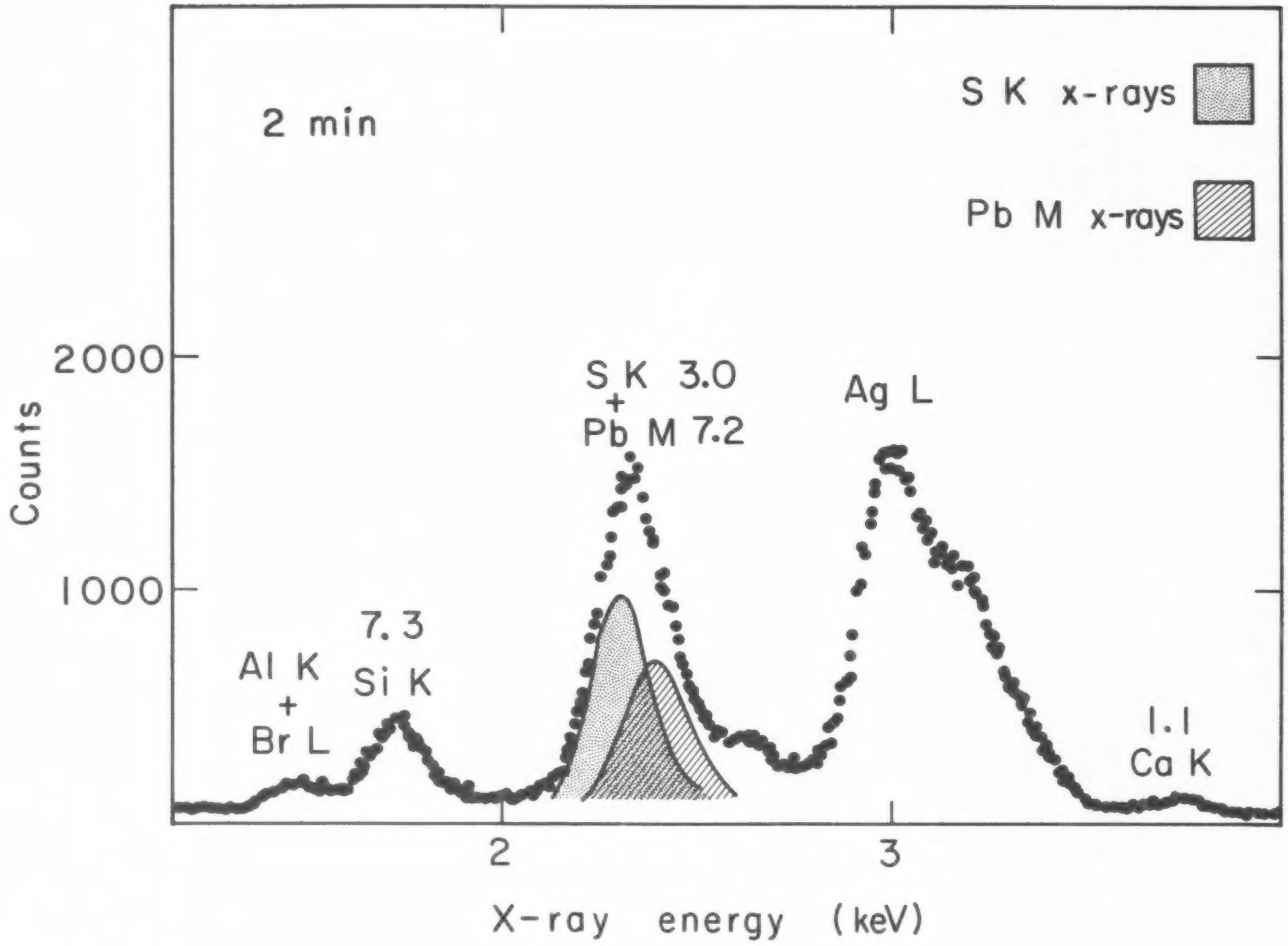

Figure 2. X-ray spectrum obtained on a 24-hr membrane filter specimen using Ag L and Bremsstrahlung excitation radiation for the determination of the elements Si, S, and Ca. Also illustrated are the overlapping S K and Pb M x-ray spectral peaks.

Typically, over 90% of the S containing particles are in the size range of 2 microns or less. This fact is substantiated in the size range of microns or less. This fact is substantiated by S data acquired on samples collected with the dichotomous air samplers and also by S data ascertained during the ACHEX programs (4), which were carried out in California during 1972 and 1973.

SPECTRAL BACKGROUND

The background under each of the x-ray lines used for analysis is referred to as the spectral background. It is related to the intensity of the scattered excitation radiation. The background arises from two sources: (1) the filter itself and (2) the beryllium window between the filter and the x-ray detector. The contribution of each of these sources is easily established by acquiring spectra from the beryllium window only, and from the window plus a blank filter. The actual particulate mass loadings collected on the filters are quite small in contrast to the mass of the blank filters.

RESULTS

Spectral data acquired for analysis are recorded on magnetic tape. Computations removing spectral background and unfolding overlapping spectral lines are made using a Control Data 6600 computer. The analysis program requires less than 40 K of core space. Element concentrations, $\mu g/m^3$, were calculated using equation 3

$$(\mu g/m^3)_i = \frac{C_i}{C_s} \times Ab_i \times \frac{m_s}{K_i} \times \frac{A}{V} \qquad (3)$$

where C_i and C_s are the characteristic x-ray count rates from element i and a thin-film standard, respectively; Ab_i is the absorption correction (for automotive particulate loadings); m_s is the mass of the standard, $\mu g/cm^2$; K_i is the ratio of the x-ray system sensitivity factor for element i to that of the standard element; V is the air volume sampled, m^3; and A is the area, cm^2, over which the particulate deposit is collected on the filter.

Typically, analyses were carried out using two 2-minute counting periods. Analytical results, including errors due to counting statistics, were put on punch cards. A control sample was analyzed each day as check of the x-ray system. Analytical results determined for six elements: Si, S, Ca, Fe, Br, and Pb, for which counting statistics were not the limiting factor, were reproducible to within ± 4%.

Additionally, quality assurance analyses have been made on 13% of the aerosol specimens collected on membrane and cascade after filters. This was achieved by determining the concentrations of five elements: Ca, Fe, Zn, Br, and Pb, using a different x-ray spectrometer. Agreements to within 5% were typically obtained when counting statistics were not the limiting factor. Quality assurance analysis for elements with low energy x-rays: Si, S, and Cl, was not possible with the second x-ray system.

Also, due to the small size limitations of dichotomous filter specimens (15-mm OD punched out discs), quality assurance analyses could not be carried *out using the other x-ray spectrometer.*

Correlations among four pairs of elements have been observed. Tables II and III list correlations established for air particulate specimens collected on membrane filters between January 1976 through March 1976. For this time period, 96 specimens were analyzed. Ratios and correlations established between Ca/Si and Fe/Si are in very close agreement with data reported by Flocchini et al. (5).

A comparison was made betwwen XRF S data and wet chemical methylthymol blue sulfate data for 4-hr and 24-hr aerosol specimens collected on membrane filters during the period 1/13/76 to 6/29/76. The data for the 4-hr samples are shown in Figure 3. A linear regression of the 219 data points yields the equation $S - 0.32 \times SO_4^{=} + 0.08$ *with a coefficient of determination of 0.95.*

For the 24-hr samples, 56 data points were used and are shown in Figure 4. (Data for 33 additional specimens were not included as they had varying degrees of brown spots on the reverse side of the filter. This can be attributed to condensation getting onto the filter. In such cases, sulfate is absorbed into the filter and low XRF sulfur data is realized.) A linear regression yielded the equation $S = 0.29 \times SO_4^{=} + 0.27$ *with a coefficient of determination of 0.93. For these specimens the XRF sulfur data could be slightly low due to heavier particulate loadings which increase x-ray absorption effects.*

At the sites used for the study, maximum levels of particulate S due to emissions from vehicles equipped with catalytic converters is estimated. Data obtained for the 24-hr air particulate specimens collected on Anderson cascade after filters (particles < 0.7) were used for the estimation. Paired sets of samples collected at site A (approximately 30-m back and 1-m above the west side of the San Diego freeway) and at site C (approximately 8-m back and 1-m above the east side of the freeway) between 7/15/75 and 4/6/76 were analyzed by XRF. For 38 paired sets of specimens the ratio of the difference between sulfur, ΔS, and lead, ΔPb, were plotted $((S_C - S_A)/(Pb_C - Pb_A) = \Delta S/\Delta Pb)$. *A linear regression was performed on 45 of the 48 data points. The equation of the curve obtained was* $\Delta S - 0.20 \times \Delta Pb - 0.12$ *with a coefficient of determination of 0.75. Using a value of 3.6* $\mu g/m^3$ *for Pb (this was the mean value 3.6 ± 1.6 for all cascade after filter Pb data), we obtain a S value of 0.7* $\mu g/m^3$ *or 2* $\mu g/m^3$ *as* $SO_4^{=}$. *If an estimate of 20% is used for the miles driven by vehicles equipped with catalytic convertors, an approximate average daily* $SO_4^{=}$ *impact of 9* $\mu g/m^3$ *is calculated for 100% conversion to catalytic equipped vehicles. This estimation is most likely high, as some of the particulate sulfur is produced by diesel vehicles. Also particulate sulfur can be produced by other processes (e.g., gas-particle interactions.)*

For 26 paired sets of cascade after-filter specimens collected during the time period 4/9/76 to 7/14/76, a linear regression was performed on the ΔS/ΔPb ratios. The equation of the curve obtained was $\Delta S = 0.12 \times \Delta Pb - 0.10$ *with a coefficient of determination of 0.46. This curve yields a lower* $SO_4^{=}$ *impact than the curve for the earlier time period.*

TABLE II. CORRELATIONS FOR PARTICULATE SPECIMENS

Element	Correlation with Si	Ratio to Si
Si	(1.00)	(1.00)
Ca	0.93	0.21
Fe	0.96	0.28

TABLE III. CORRELATIONS FOR PARTICULATE SPECIMENS

Element	Correlation with Pb	Ratio to Pb
Pb	(1.00)	(1.00)
Br	0.95	0.40
Zn	0.74	0.03

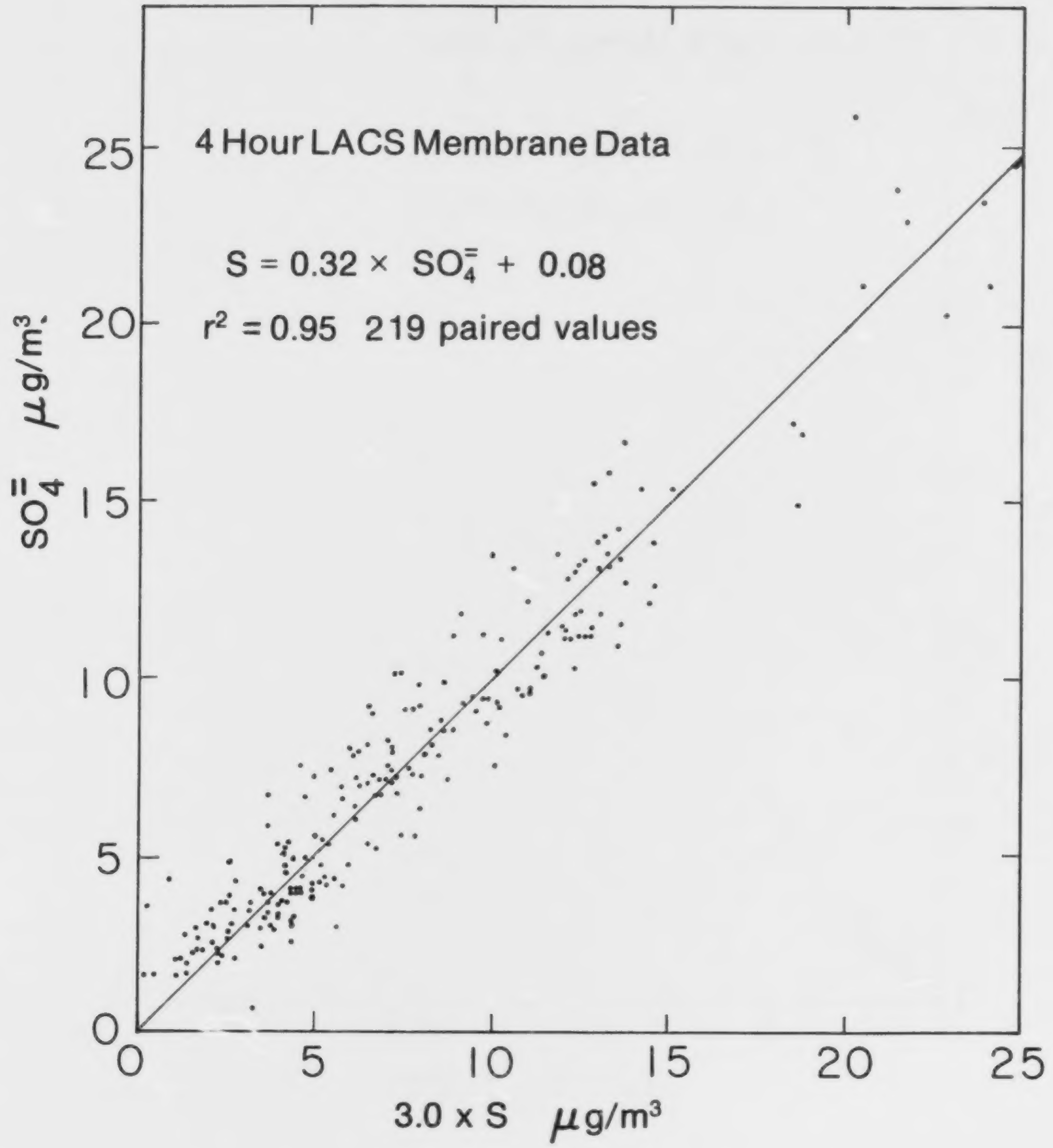

Figure 3. Comparison of XRF sulfur data with wet chemical sulfate data for 4-hr aerosol specimens collected on membrane filters.

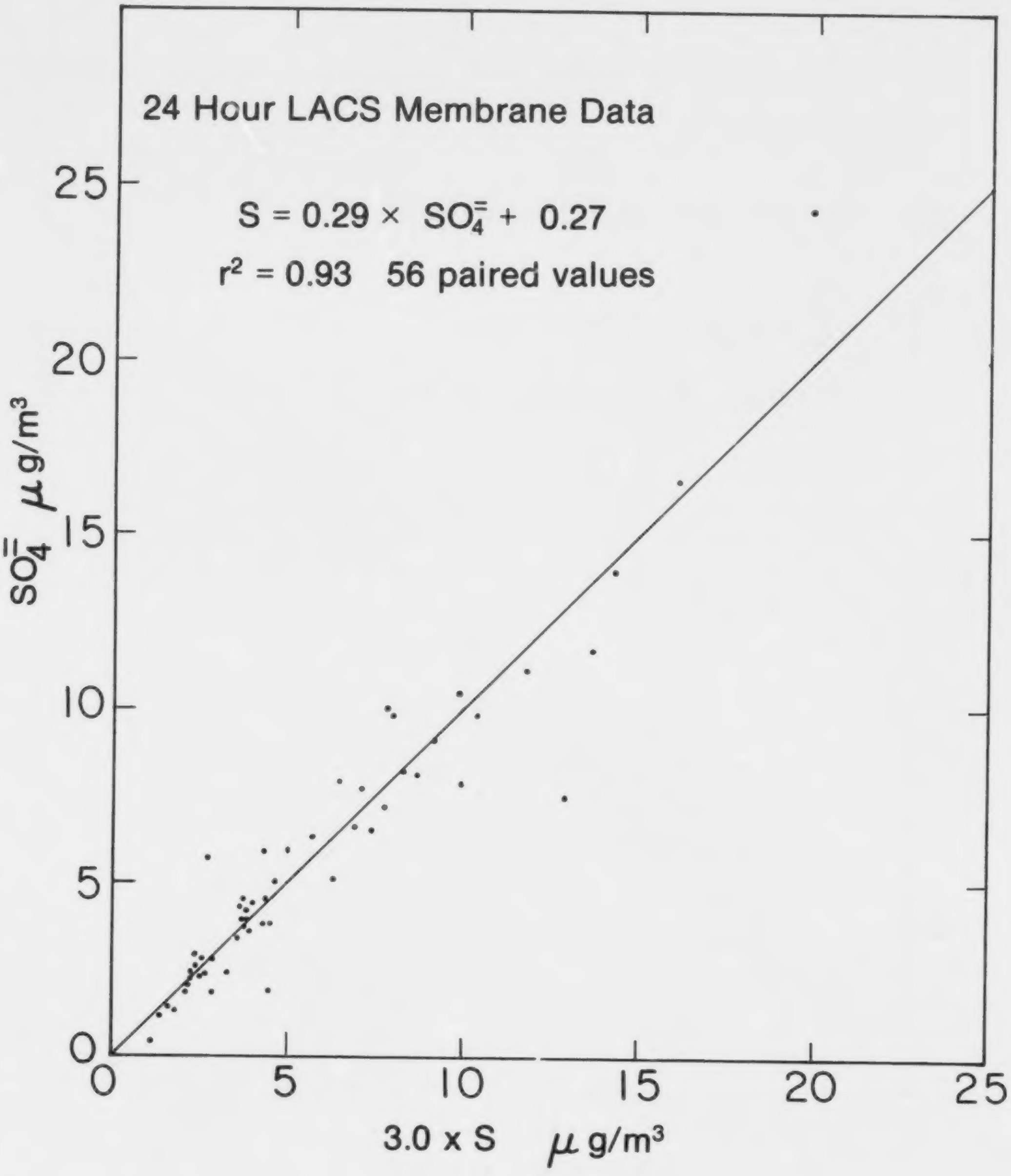

Figure 4. Comparison of XRF sulfur data with wet chemical sulfate data for 24-hr aerosol specimens collected on membrane filters.

During October and November, 1976, 15 pairs of cascade after-filter aerosol specimens were collected over 4-hr periods during peak traffic hours with the hope of amplifying any relationship which might exist between ΔS and ΔPb, but such was not evident.

Air particulate specimens collected with the dichotomous samplers were collected on 37-mm teflon filters. For XRF, 15-mm discs were cut from the edge of the deposit area. For large particle elements, Si, Ca, and Fe, the sum of the results for the two collected size fractions were usually low by a factor of 2 in contrast to total filter results. This can be attributed to non-uniform distribution of the deposit on the large particle stage. The larger particles tend to be concentrated toward the center of the filter. Similar comparisons of small particle elements: S, Br, and Pb, often had discrepancies of 10 to 20% or more.

During October 1975, air particulate specimens were collected in tandem on membrane filters. The back-up filters showed substantial losses of Cl (0.57 $\mu g/cm^2$), which is an impurity in the filter. The amount of Cl lost was the same for both 4-hr and 24-hr collection periods. Additionally, there was a small amount of S (0.05 $\mu g/cm^2$) collected on the backup filters, which could be a result of SO_2 gas interacting with the filter. Both the S and Cl x-rays are less than 3 keV. Since the XRF method only measures those x-rays which arise from the surface of the filter, the total change, for the entire thickness or mass of the filter, would be much larger.

Four blank 2.54-OD membrane filters were each washed with 50-60 ml of water, air dried, and analyzed. The Cl values decreased by 0.59 $\mu g/cm^2$. This value is in close agreement with the Cl lost in the tandem sampling experiment.

ACKNOWLEDGEMENTS

The authors are indebted to Don Malone for designing and constructing the spectrometer utilized for this study. We are grateful to Fred Goulding and members of the Electronic Research and Development Group for upgrading and maintaining the x-ray system. We thank David Gok for writing the basic computer program used.

DISCLAIMER

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FUELS SURVEILLANCE IN SOUTHERN CALIFORNIA ANALYTICAL RESULTS AND METHODOLOGY

Robert H. Jungers

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

Several constituents in fuels are of primary interest, especially those occurring naturally or those that are directly added during manufacture. These constituents include lead, sulfur, manganese, phosphorus and hydrocarbon content. Methodology for these analyses fall into one of three categories (1) available and usable, (2) available but archaic, and (3) non-existent with development necessary. Analytical data from various studies between southern California and other regions in the United States as well as current analytical methodology is discussed.

INTRODUCTION

The advent of the catalyst equipped vehicle which requires the use of unleaded gasoline initiated the surveillance of motor vehicle gasoline specific to the Los Angeles area. Initial interest focused on sulfur in gasoline as a possible contributor to atmospheric pollution from engine emissions. Next, attention was directed to lead and phosphorus content of unleaded gasoline, a known poison from vehicle catalysts. Unleaded gasoline by definition has limited lead content, with an allowed maximum of 0.05 grams lead per U.S. gallon (g Pb/gal). Phosphorus must be limited to a maximum of 0.005 grams per U.S. gallon (g P/gal). Presently interest has expanded beyond these areas to include consideration of aromatic content, manganese content and other factors. Development of new and more efficient analytical methodology was facilitated by widespread interest in having more available data coupled with the constraint of a non expandable workforce.

DISCUSSION

ANALYTICAL

Table I shows the result of 136 unleaded gasoline samples collected nationwide in the summer of 1974. The average sulfur content is 0.028 weight percent (wt. %S) with Region IX (San Francisco) having an average value of 0.018 wt.%S. Table II represents sulfur data from 140 samples taken in New York State (NYS) from NYS police vehicles during 1976. These vehicles are fueled from regular service stations along the NYS throughways. The average

TABLE I. SULFUR IN UNLEADED GASOLINE SUMMER & FALL 1974

TOTAL SAMPLES 136

CONCENTRATION 0.028 weight percent sulfur

REGION	NO. OF SAMPLES	SULFUR WT. %
I	24	0.029
II	14	0.023
V	22	0.031
VI	23	0.035
VII	22	0.037
VIII	23	0.023
IX	8	0.018

TABLE II. NEW YORK STATE FUELS SURVEY SULFUR IN UNLEADED GASOLINE DECEMBER 1975 to NOVEMBER 1976

Date		No. Samples	Avg. Sulfur (wt percent)
Dec.	1975	10	0.0161
Jan.	1976	10	0.0152
Feb.	1976	10	0.0136
Mar.	1976	10	0.0176
Mar/Apr	1976	10	0.0172
Apr/May	1976	10	0.0208
May	1976	10	0.0199
May/Jun	1976	10	0.0152
Jun.	1976	10	0.0178
Jul/Aug	1976	10	0.0186
Aug/Sept	1976	10	0.0208
Sept/Oct	1976	10	0.0162
Oct/Nov	1976	10	0.0180

Sample Number - 140

Average Value - 0.017% Sulfur

Range - 0.006 to 0.043% Sulfur

sulfur content is shown as 0.017 wt.%S. This value should be compared with the average values of sulfur as shown in Table III for California. This Table compares sulfur content of gasoline sampled in Los Angeles and San Francisco at the same time in 1975. The average sulfur content of unleaded gasoline ranges from 0.027 wt.%S in San Francisco to 0.034 wt.%S in Los Angeles. This is nearly double the previously presented New York average of 0.017 wt.%S. The analyses of both the regular leaded and premium leaded gasoline grades collected in Los Angeles and San Francisco indicate higher sulfur content in Los Angeles. Table IV presents data from unleaded gasoline sampled in southern California between January and July 1976. The average sulfur value is 0.026 wt.%S with a monthly average range of 0.019 to 0.036 wt.%S. The average lead value is 0.005 g Pb/gal with a monthly average range of 0.003 to 0.008 g Pb/gal. The average aromatic value is 42.7% with a monthly average range of 33.6% to 46.3%. Aromatic content of gasoline is of great importance to both the refiner and the environmentalist. Higher aromatic content can increase the octane number of the gasoline. As organic metallic fuel additives are reduced the addition of aromatics is one way to keep the octane number up and avoid the customer complaint of "spark knock." The environmentalist sees the increase in aromatics as a potential health hazard. Table V and Table VI present an analytical comparison of gasolines collected in Los Angeles and San Francisco during the winter of 1975-1976 and the summer of 1976. It should be noted that on the the whole the sulfur content is higher in the Los Angeles samples and that the aromatic content is higher in the summer than winter.

METHODOLOGY

A summary of analytical methodology as used in our laboratory is shown in Table VII. Three separate groupings are listed: one, methods available and used; two, methods available but extremely slow and tedious; and three, methods developed in house which are designated as American Society of Testing and Materials (ASTM) standard methods, potential ASTM standard methods and survey methods used to expedite analyses for regulatory support.

The sulfur method by gas chromatograph flame photometric detector (GC/FPD) has increased our capability by at least a factor of five, 12 to 60 samples per day. The phosphorus method using the flameless atomic absorption spectrometer with a graphite furnace (AAS/HGA) is capable of surveying 80 samples per day while 10 samples per day by the molybdate-hydraine method is average. Table VIII indicates a comparison between the AAS/HGA and the molybdate-hydrazine method in iso-octane standards. Figure 1, a bar graph, presents a comparison of 45 unleaded gasoline samples by both methods. The molybdate-hydrazine method indicated all samples to be 0.001 g P/gal. while the AAS/HGA method showed the following phosphorus content distribution.

27-0.001
7-0.002
5-0.003
1-0.004
5-0.005

Both methods indicate that the 45 samples are at or less than 0.005 g P/gal. This is the maximum amount allowed in unleaded gasoline. Therefore, this is

TABLE III. COMPARATIVE STUDY OF GASOLINE IN REGION IX FOR SULFUR CONTENT
SUMMER 1975

GRADE	HIGH	LOW	AVG.	NO. OF SAMPLES
		SAN FRANCISCO BASIN		
Premium	0.024	0.001	0.009	19
Regular	0.094	0.003	0.035	15
No Lead	0.068	0.003	0.027	18
		LOS ANGELES BASIN		
Premium	0.062	0.002	0.024	19
Regular	0.090	0.033	0.051	12
No Lead	0.085	0.010	0.034	16

All results reported in weight percent sulfur.

TABLE IV. SOUTHERN CALIFORNIA UNLEADED GASOLINE FUELS SURVEY
JANUARY - JULY 1976

Month	No. of Samples	% S	Avg. Values g Pb/gal	% Aromatics
JAN	2	0.027	0.007	33.6
FEB	3	0.033	0.007	42.3
MAR	27	0.020	0.005	42.2
APR	5	0.036	0.008	46.3
MAY	16	0.031	0.005	42.7
JUN	14	0.028	0.006	43.3
JUL	3	0.019	0.003	45.7

TABLE V. MVMA FUEL SURVEY
Winter 1975 - 1976

LOS ANGELES	% S	g Pb/gal	RON	% Aromatics
Prem Pb				
Hi	.107	3.830	99.2	34.8
Lo	.018	.790	93.8	23.4
Avg.	.043	2.237	98.0	28.8
Reg Pb				
Hi	.145	2.050	96.0	32.7
Lo	.006	.370	93.1	23.3
Avg.	.052	1.259	94.0	27.4
No Lead				
Hi	.058	.007	96.1	37.3
Lo	.006	.002	90.8	27.5
Avg.	.025	.004	92.3	32.7
SAN FRANCISCO				
Prem Pb				
Hi	.021	3.670	100.2	37.4
Lo	.002	1.180	96.4	18.6
Avg.	.014	2.277	98.6	28.4
Reg. Pb				
Hi	.081	1.970	95.9	32.8
Lo	.007	.420	93.2	23.9
Avg.	.035	1.331	94.4	27.1
No Lead				
Hi	.038	.015	96.6	38.6
Lo	.002	.003	91.1	19.6
Avg.	.017	.007	92.9	30.6

TABLE VI. MVMA FUEL SURVEY
Summer 1976

Los Angeles	% S	g Pb/gal	RON	% Aromatics
Reg. Pb				
Hi	.143	2.810	94.1	35.4
Lo	.029	0.520	92.0	23.7
Avg.	.066	1.487	93.3	31.0
No Pb				
Hi	.048	.007	95.8	44.1
Lo	.012	.001	91.0	26.9
Avg.	.026	.004	92.6	34.1
SAN FRANCISCO				
Reg. Pb				
Hi	.077	3.360	95.3	34.7
Lo	.016	.600	93.7	25.7
Avg.	.042	2.056	94.4	28.9
No Pb				
Hi	.046	.018	96.2	42.5
Lo	.012	.001	91.5	28.5
Avg.	.030	.006	92.9	33.8

TABLE VII. ANALYTICAL METHODS

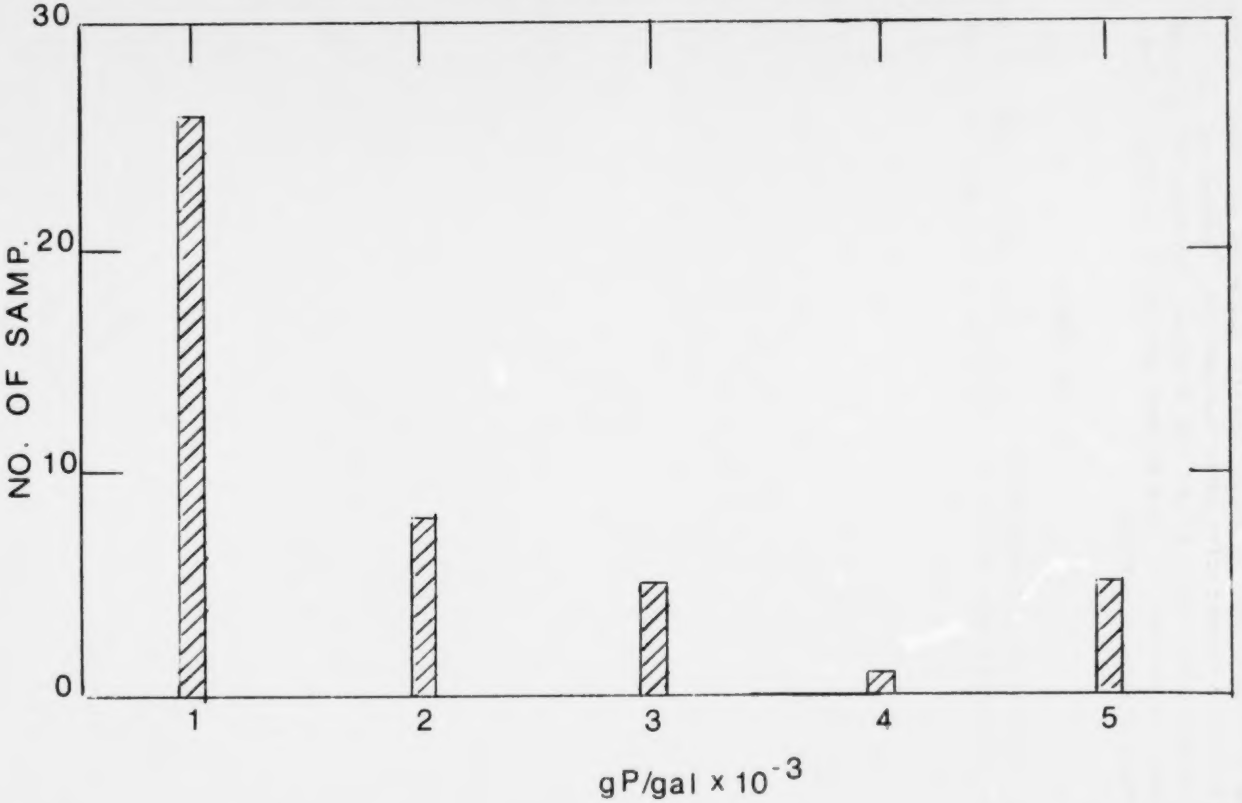
I	Available and Used		
	Fluorescent Indicator Absorption	ASTM	D - 1319
	DEPENTANIZATION	ASTM	D - 2001
	API Gravity @ 60°F	ASTM	D - 287
	Reid Vapor Pressure	ASTM	D - 323
	DISTILLATION	ASTM	D - 86
	Sulfur, Lamp	ASTM	D - 1266
II	Available - Slow and Tedious		
	Sulfur, Lamp	ASTM	D - 1266
	Phosphorus, Colormetric	ASTM	D - 3231
	Lead, Gravimetric	ASTM	D - 526
III	Developed In-House		
	Lead, AAS	ASTM	D - 3237
	Lead, FTK	ASTM	D - 3348
	Sulfur, GC/FPD		
	Phosphorus, AAS - HGA		
	Manganese, AAS.		

TABLE VIII. COMPARISON OF AAS/HGA MOLYBDATE-HYDRAZINE METHODS

G/GAL P MOLYBDATE-HYDRAZINE METHOD	*G/GAL P HGA SCREENING METHOD*	
.002	*.004*	*REPLICATE*
.002	*.004*	
.002	*.002*	
.002	*.002*	
.001	*.002*	
.001	*.001*	
.001	*.002*	

MOLYBDATE-HYDRAZINE VS. SCREENING METHOD USING ISO OCTANE STANDARDS

Figure 1. Phosphorus in gasoline HGA screening method.



considered to be an acceptable screening method. Manganese as an antiknock additive has become increasingly attractive to refiners as lead content is reduced by law. The manganese additive, Ethyl MMT or methyl cyclopentadienyl manganese tricarbonyl, is in ever increasing use. The present recommended use by Ethyl is 0.0625 g Mn/gal or 1/16 g Mn/gal. Table IX presents comparative data obtained by additions to unleaded gasoline at the low end of concentration. Comparative data between our method and the method used by Dupont showed comparability at the average recommended concentration. This method and variations of this method are being collaboratively tested by ASTM as a future standard method.

CONCLUSION

Our laboratory is confident that as the need arises for more data on fuels and fuel chemistry analytical methodology we can meet this challenge.

TABLE IX. RECOVERY OF SOLUBILIZED AQUEOUS MANGANESE STANDARDS FROM GASOLINE

BRAND	LOCATION	GMS/GAL AMOUNT ADDED	GMS/GAL AMOUNT RECOVERED
ARCO	OREGON	0.004	0.004
CITGO	TEXAS	0.001	0.001
PHILLIPS 66	N. CAROLINA	0.004	0.003
TEXACO	TEXAS	0.004	0.003
MARATHON	INDIANA	0.001	0.001
EXXON	NEW YORK	0.001	0.001
STANDARD	GEORGIA	0.001	0.001
UNION 76	CALIFORNIA	0.001	0.001

COMPARISON OF DUPONT & MOLECULAR CHEMISTRY LABORATORY METHODS

GRAMS PER GALLON MANGANESE DUPONT METHOD	GRAMS PER GALLON MANGANESE MOLECULAR CHEMISTRY METHOD
0.078	0.072
0.026	0.032

MEGAVOLUME SAMPLER (MARK I) FOR COLLECTING RESPIRABLE PARTICULATES AT THE LACS SITE

Ralph I. Mitchell and W.M. Henry

Battelle, Columbus Laboratories
Columbus, Ohio

ABSTRACT

A large volume sampler for the collection of gram quantities of respirable particulates has been designed and calibrated. The sampler, which is being used at the Los Angeles Catalyst Study site, has a daily sampling rate of approximately 1,000,000 cubic feet (28, 143 m^3) and has two impactor stages with cutoff sizes of 3.6 and 2.1 μm. Particulates smaller than 2.1 μm are collected on high purity aluminum precipitator plates which are removable for sample recovery. The main advantages of the sampler are that samples are collected in three size fractions, there is minimal contamination from the collection substrate, and samples are partitioned into respirable fractions of sufficient size for detailed chemical analysis and bioassay screening.

INTRODUCTION

The hazard associated with the inhalation of airborne particulates depends upon their physical, chemical and/or biological properties. These properties determine their deposition site within the respiratory tract and their interaction after they have been deposited. One of the major mechanisms for particle removal within the lung is by ciliary action. Non-soluble particles which penetrate beyond the ciliated portion of the lung ("respirable particulates") will remain in contact with the lung tissue for extended time periods and consequently may be capable of producing very deleterious effects.

In order to correlate potential health hazards of air pollutants with epidemiological data, it is necessary to not only have a sampler which has size-selecting characteristics of the human respiratory tract but one which will collect a sample large enough for detailed chemical analysis with minimal contamination from the collection substrate. The quantity of particulates collected in most 'respirable' dust samplers is not sufficient for bioassay and, for many of the trace materials, more of the specific component can be found in the collection substrate than in the collected sample. The sampler described herein has a sampling rate of at least 15 times greater than commercially available samplers. (1,2) and the total sample is collected either on a Teflon or high purity aluminum substrate which minimizes any potential contamination.

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Another major advantage to this sampler is that the collection characteristics of the first stage duplicates the ACGIH (3) respirable curve. The other samplers which use this distribution as their design criteria have limited sampling rates (4, 5), and the sample fraction of interest is collected on a filter substrate.

Because of the urgency of the catalyst problem the megavolume samplers were taken to the Los Angeles Catalyst Study (LACS) site before they were thoroughly evaluated and calibrated in the laboratory. However, over one year of operation has been obtained with the original prototype sampler and the experience obtained has shown several design changes which would improve the ease of operation of the sampler. The current version of the sampler (Mark II) has incorporated these design changes. This paper presents some of the calibration and collection data of the LACS sampler as well as some of the collection data with the Mark II version to show some of the overall merits of such a sampling system.

DESCRIPTION OF SAMPLER

The sampler body is constructed of stainless steel and is approximately 4-1/2 feet tall and 2 feet square. Figure 1 is a photograph of one of the LACS samplers located beside the San Diego Freeway. Figure 2 is a schematic diagram which shows the principle of operation. The sampler is essentially a large cascade impactor which utilizes an electrostatic precipitator to collect the fines which are not impacted on the last collection stage. Air is pulled through the sampler by means of a 1000 cfm high pressure blower; however, the flow characteristics of the blower are such that the total flow is reduced to 690 cfm with the operating pressure drop. The blower is driven with a 1 hp motor which pulls up to 12 amperes at 115 volts.

Air enters the sampler at the top perimeter which serves as the scalping stage and has a cutoff size of approximately 20 μm. The air then enters the impaction plate assembly containing four 16-gage stainless steel plates with slots which serve as impactor jets and collection targets. The first two plates have a cutoff size of 3.6 μm. The jet stage has 110 slots which are 1/4 x 1 inch with rounded corners. The distance between the collection stage and the jet stage is 1/2 inch and the target width is 1-1/8 inch. The next two plates (second stage) have a cutoff size of 2.1 μm and they are 1/8 of an inch apart. The jet stage consists of 374 rectangular slots 1/16 x 1 inch. The impaction surface for each slot is 7/16 of an inch wide. The impaction plate assembly is constructed of anodized aluminum and can be disassembled by the removal of two screws holding an end plate. Both the impaction jets and collection plates are Teflon coated to minimize substrate contamination of the sample. This also facilitates in the removal of the sample.

After passing through the impaction plates, the smaller particles are collected by means of a specially designed precipitator plate assembly which accommodates for ready removal of the plates for sample recovery. These are 55 high purity aluminum collector plates approximately 11 x 17 inches and in the latest version these are coated with a conducting Teflon film.

There is a precipitator ionizing section which has a positive potential

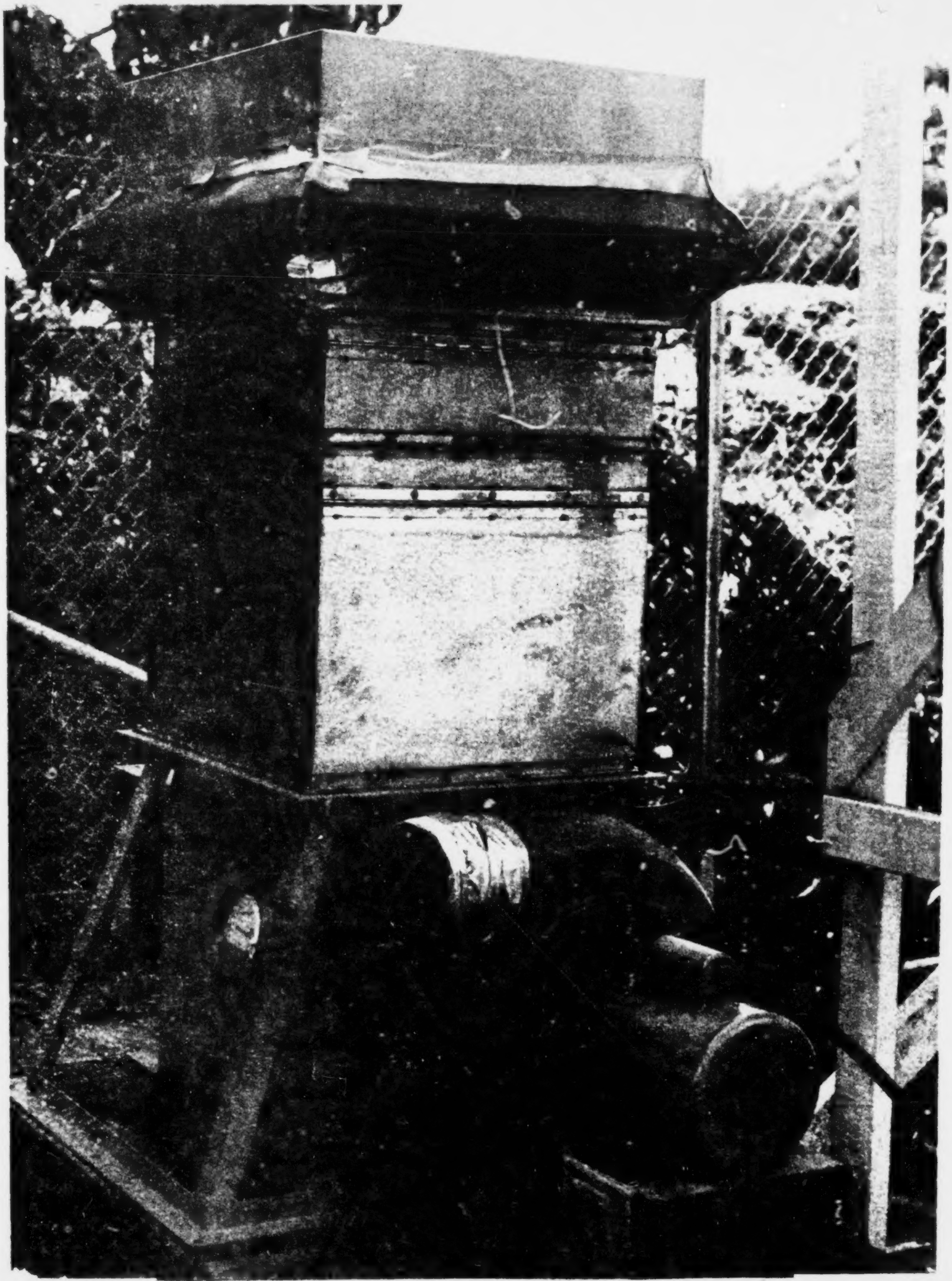

Figure 1. Megavolume sampler located at a LACS site.

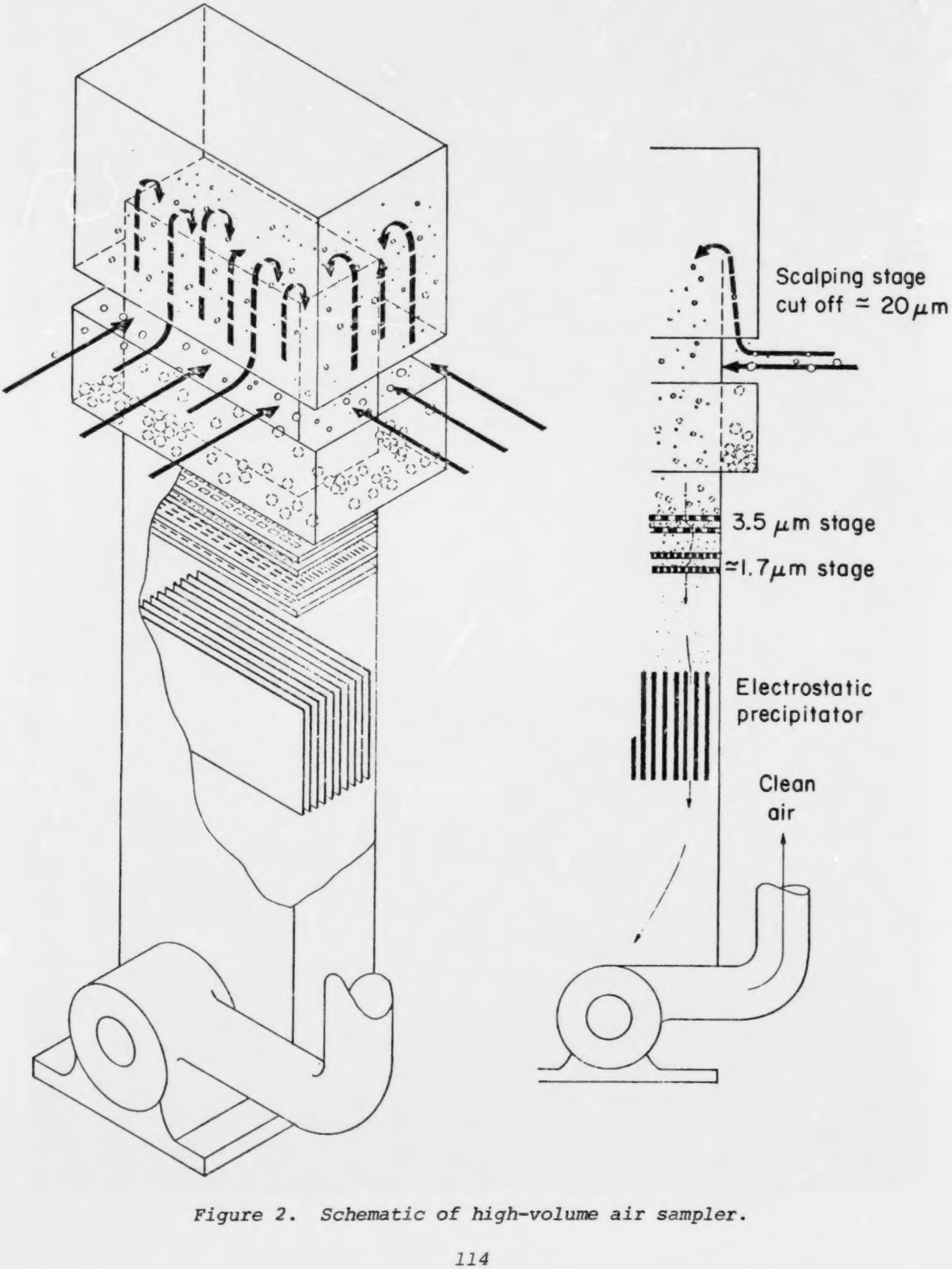
Scalping stage
cut off ≈ 20 μm
3.5 μm stage
≈1.7μm stage
Electrostatic
precipitator
Clean
air

Figure 2. Schematic of high-volume air sampler.

of approximately 8000 volts. The precipitator plates also carry the same voltage and each plate alternates from positive to negative. The clean air passes through a transition section which connects directly to a high pressure blower.

CALIBRATION OF IMPACTOR STAGES

The main criterion of this sampler was to have the collection characteristics of the first stage duplicate or closely approximate the ACGIH respirable curve. In order to obtain the high volumes required, it was necessary to use long slots. The impaction characteristics of these slots were determined by means of a miniature impactor which would accommodate either one or two slots of the same size of those to be used in the full-scale sampler. This impactor was designed so that the jet-to-slot spacing could be varied over a wide range. Particulates which did not impact on the impaction stage were collected on a 142-mm glass fiber backup filter.

The impaction efficiency curves for the impactor jets were determined using monodispersed aerosols of dibutyl phthalate containing a highly fluorescent dye. The aerosols were generated using a Bergman-Liu generator and the particles were passed through a heated duct to insure complete evaporation of the diluting solvent (ethanol). The particle size of the aerosol was continuously monitored by sampling with a cascade impactor. The impactor sampling showed that the aerosols were monodispersed and in the approximate size range. The impactor slides were coated with "Aerosol OT" and the exact size of the droplets before impact could be determined with a microscope knowing the flattening coefficient of the droplets.

Figure 3 show the impaction characteristics of the 1/4 inch by 1 inch slots used in the first stage of the megavolume sampler. This figure shows the effect of changing the target width from 1/2 to 1 1/8 inch. With the 1 1/8 inch wide impaction target the impaction parameter, $\Psi^{1/2}$, was found to be 0.35 which yields a cutoff size of 3.6 μm. The impaction parameter, $\Psi^{1/2}$, for the second stage which has a target surface which is 7 times wider than the jet width is 0.45. It produces a cutoff size of 2.1 μm.

FIELD COLLECTION DATA AND COMPOSITION ANALYSIS

The following presents the results obtained from the first four days of use of the sampler at the LACS site. One sampler was placed upwind and the other sampler placed on the downwind side of the freeway. During this sampling period a 24 hour sample was taken at each site with a special Battelle cascade impactor which was designed for the particle size determinations of automobile exhaust.

Table I shows the weights obtained for the collection stages for the two sampling sites. The data show that the particulate concentration of the air at the down stream site is about 20 percent greater than at the upstream site.

Figure 4 shows the particle size distribution of the pollutants at the upstream site obtained with the special cascade impactor. Figure 5 shows similar data obtained at the down stream site. On both of these figures the

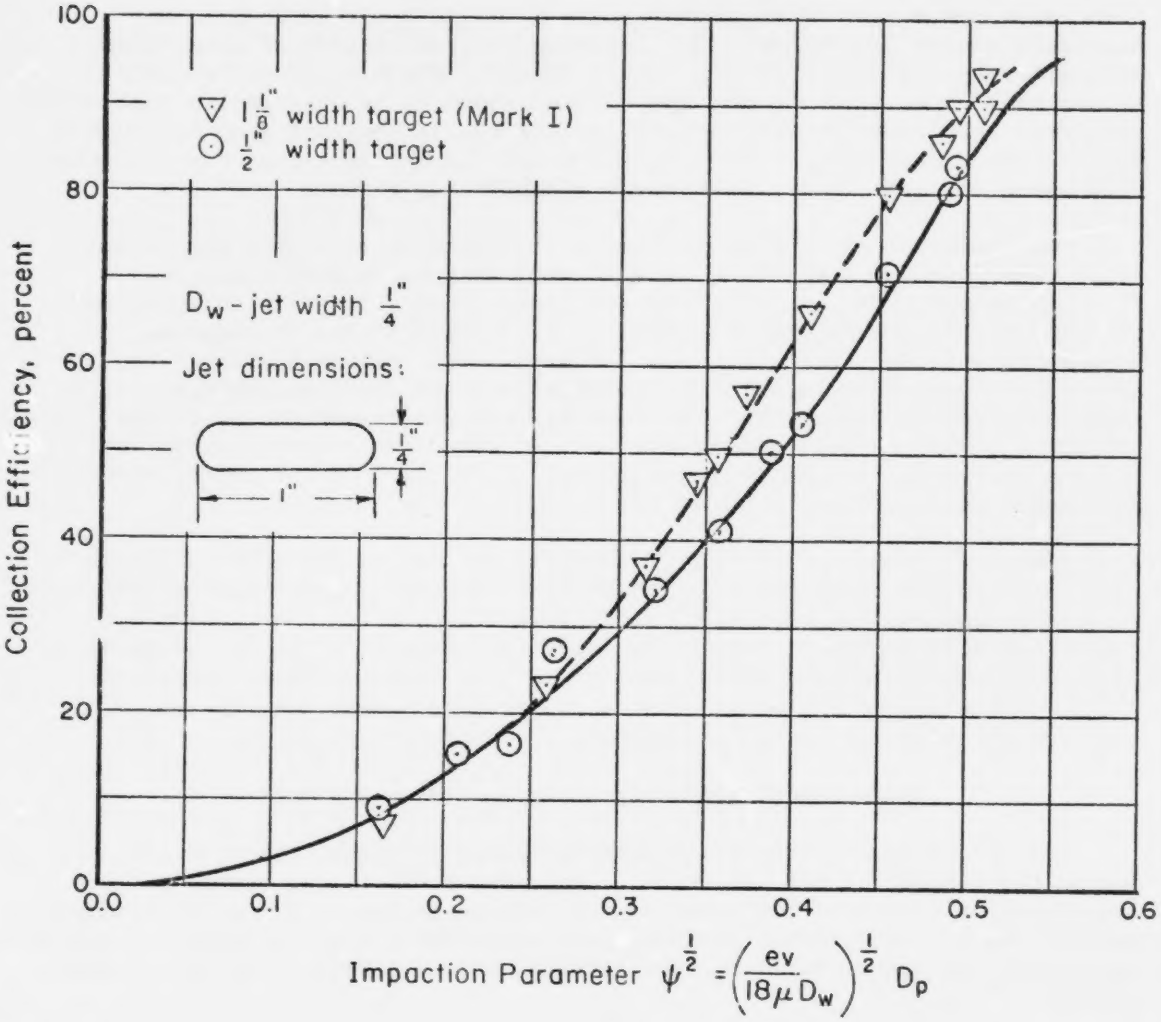

Figure 3. Impaction efficiency curves for 1/4-inch wide jets.

TABLE I. PARTICULATE COLLECTION AT L.A. SITE

Site Location	Size Fraction	Time Period	Mass, g	Percent
Site A (Upwind)	3.6-20 µm (first stage)	∿4 days (100 hr)	1.440	25.5
	2.1-3.6 µm (second stage)	∿4 days (100 hr)	0.845	14.9
	<2.1 µm (electrostatic plates)	∿4 days (100 hr)	3.370	59.6
	TOTAL		5.655	100.0
Site C (Downwind)	3.6-20 µm (first stage)	∿4 days (100 hr)	1.245	18.6
	2.1-3.6 µm (second stage)	∿4 days (100 hr)	0.945	14.2
	2.1 µm (electrostatic plates)	∿4 days (100 hr)	4.495	67.2
	TOTAL		6.685	100.0

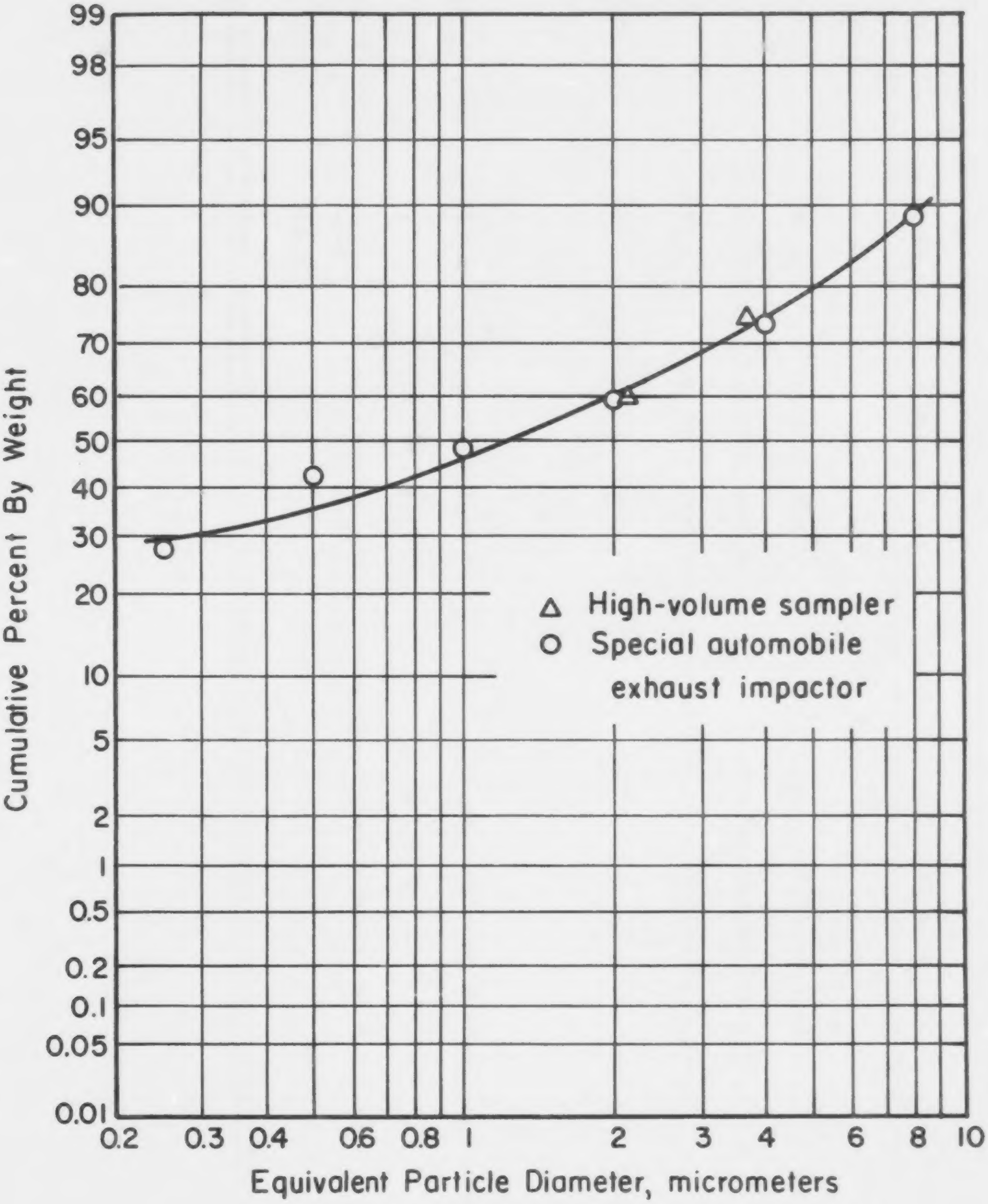

Figure 4. Particle size distribution of upwind pollutants at San Diego Freeway site.

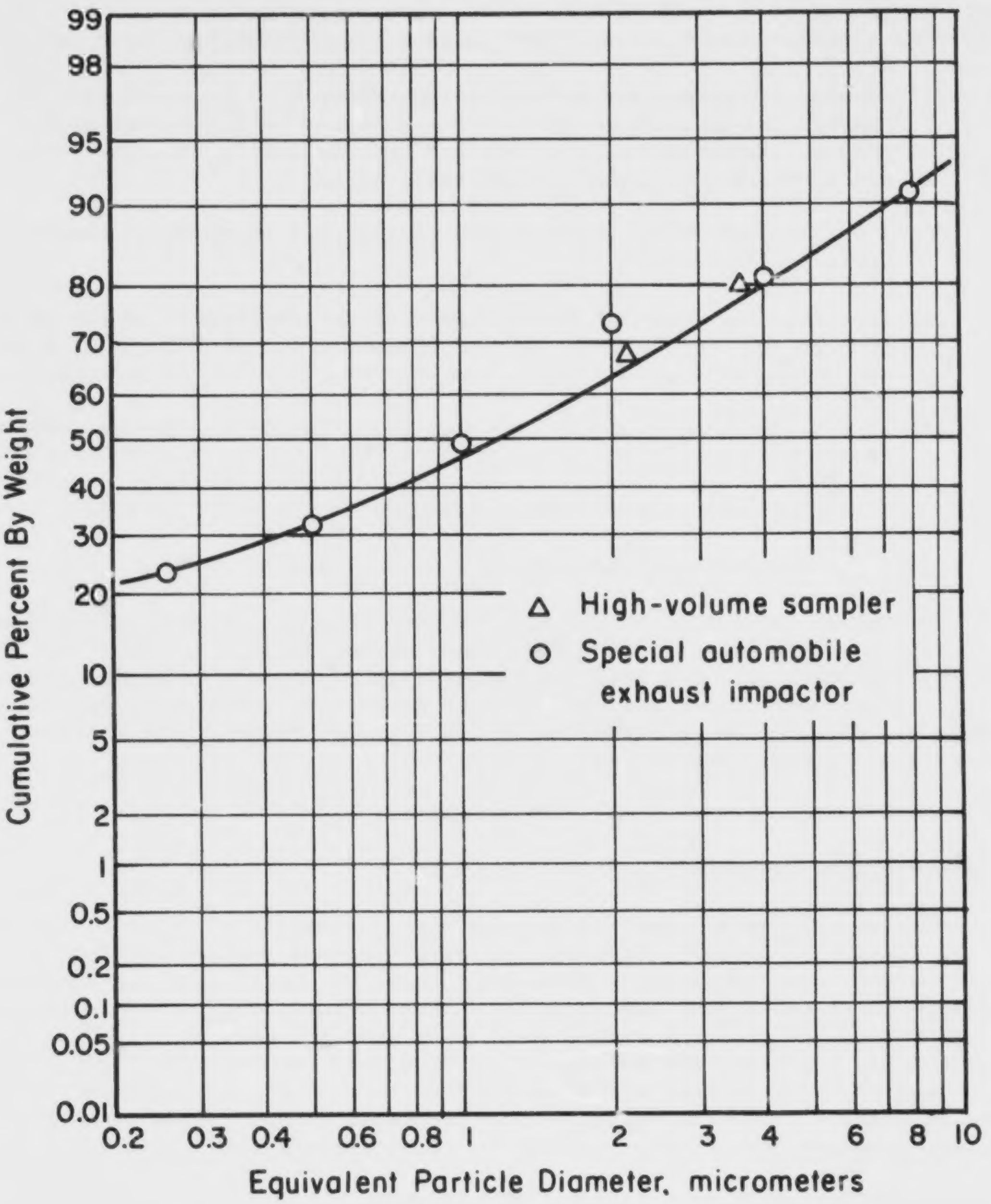

Figure 5. Particle size distribution of downwind pollutants at San Diego Freeway site.

data obtained with the megavolume sampler is shown. In both cases the particle size data obtained with the megavolume sampler agrees with that of the special cascade impactor.

Table II shows some preliminary chemical analysis obtained with these samples. Since these samples were taken, several pounds of sample have been collected. The tentative conclusions which can be drawn from these data are:

(1) Several elements show concentration change with size. Those of crustal origin such as Iron (Fe) are higher in the larger size ranges. Those of man's activities such as Sulfur (S), Lead (Pb) and organics are higher in the small sizes.

(2) A traffic effect is shown by the Pb contents of downwind versus upwind collections.

(3) Nitrite (NO_3^-) accounts for ∿70 percent (weight basis) of the total Nitrogen (N) in the large particle size while ammonium (NH_4^+) accounts for ∿75 percent of the total N of the very fine (>2.1 um sizes.)

(4) Sulfate ($SO_4^=$) accounts for most of the S in the two larger particle sizes, while the total S, before and after benzene extraction, and the $SO_4^=$ to total S ratio in the fine fraction indicates possibly 1 to 2 percent organo sulfur compounds in the < 2.1 μm size.

COLLECTION CHARACTERISTICS OF THE MARK II SAMPLER

The second generation of the sampler has incorporated most of the design limitations of the prototype sampler which evolved during its field use. The major problem area has been the reliability of the electrostatic power supply. This part of the sampler has been completely redesigned. Another change has been in the cutoff sizes of the impactor stages. The current cutoff sizes are 3.5 and 1.7 μm.

REPRODUCIBILITY

REPRODUCIBILITY TESTS USING AMBIENT AEROSOLS

In order to check repeatability and reproducibility of the two samplers in the field with ambient aerosols, the samplers were positioned about 20 feet apart outside the laboratory. Because of building obstruction and possible variance in meterological condition, the sampler positions were interchanged daily in order to minimize sample bias. The samplers were operated for 14 days. Table III shows the weights of particulates removed from each collection surface. The alcohol scrub was used to recover any particulate residue left on Stage 3 after the normal scrape recovery. These results show that the two samplers have similar collection characteristics.

REPRODUCIBILITY TESTS WITH FLUORESCENT AEROSOLS

After determining that essentially identical data could be obtained with the full-scale sampler as compared with single slots, the sampler was

TABLE II. ANALYSES OF COLLECTED PARTICULATES FROM L.A. BACKGROUND CATALYST STUDY SITE - RESULTS IN PERCENT

Site A		Pb	Total S	Fe	Benzene-Soluble Organics	S [(a)]	$SO_4^=$	C	H	N	NO_3^-	NH_4^+
Upwind:	First Stage	0.86	2.0	3.6	8.0	2.4	6.45	7.3	1.5	2.2	7.75	0.87
	Second Stage	1.13	5.6	2.9	9.0	6.5	16.8	7.9	2.4	2.5	2.85	2.55
	Electrostatic	0.93	8.7 [8.9] (b)	1.0	16.6	9.4	21.3	6.5	4.3	3.1	6.5	3.55
Site C												
Downwind:	First Stage	2.43	2.0	3.8	4.3	1.9	6.3	8.6	1.7	1.9	7.4	0.69
	Second Stage	3.16	4.7	3.1	8.8	5.2	14.6	10.6	2.3	2.3	5.5	2.17
	Electrostatic	3.74	5.5	1.9	16.0	6.1	17.4	9.4	3.4	2.5	3.0	2.45

(a) After benzene extract.

(b) Recheck determination.

TABLE III. REPRODUCIBILITY OF THE MARK II SAMPLERS IN THE COLLECTION OF AMBIENT AEROSOLS

	Sampler A	Sampler B
1st Impactor Stage (3.5 to 20 μm)	1.177 g	1.074 g
2nd Impactor Stage (1.7 to 3.5 μm)	0.996 g	0.995 g
3rd ESP Stage (<1.7 μm)	9.110 g	9.073 g
Alcohol Scrub of Precipitator Plates	0.800 g	0.860 g
Total	12.083 g	12.002 g

challenged with a fluorescent aerosol. The aerosol was generated by means of a conventional aerosol can containing the dye dissolved in Freon.

The aerosols were sprayed into the wind tunnel containing the massive volume samplers and a special cascade impactor. A high-volume filter sampled the effluent from the megavolume samplers in order to obtain the overall collection efficiency.

Figure 6 is a particle size distribution plot of the fluorescent aerosol generated by Can "E" as obtained by the Battelle cascade impactor. This plot shows that the mass median diameter of the aerosol is 2.8 μm. The plot also shows the two data points obtained with the massive volume samplers. Twenty-eight percent of the aerosol mass was collected on Stage 1 (3.5 μm) and the cascade impactor distribution shows about 32 percent is larger than that size. This is very good agreement considering some of the material is removed by the scalping stage. The second data point for 1.7 μm fell exactly on the distribution curve (78 percent of the particles were larger than that size).

COLLECTION EFFICIENCY OF PRECIPITATOR UNIT

Another change in the megavolume sampler was to switch from a positive to a negative ionizing corona and to coat the precipitator plates with a conducting type Teflon to minimize the difficulty in removing the collected particles from the precipitator plates. The collection efficiency of the megavolume sampler containing Teflon-coated percipitator plates was determined with the Minnesota aerosol analyzing system. Ambient air was sampled and the particle concentration was measured at the sampler inlet and outlet.

Figure 7 is a plot of the collection efficiency obtained over the particle size range of 0.013 to 0.75 μm. This plot shows that the average collection efficiency for the submicron particles is over 90 percent. For this test the voltage on the precipitator plates was 5500 and the ionizing wire carried a negative potential of 10,000 volts.

CONCLUSIONS

The massive volume sampler provides a means by which gram quantities of particulates can be collected from low concentration ambient atmospheres. The collected particulates are classified according to the ACGIH criteria for respirable aerosols and there is a further classification to separate the primary and secondary aerosols. The sampler has a high collection efficiency and minimizes the possibility of contamination from the collection substrate. Samples obtained using this collector are ideally suited for an iterative biological-chemical testing scheme for the identification of possible causative agents for airborne insult to human health.

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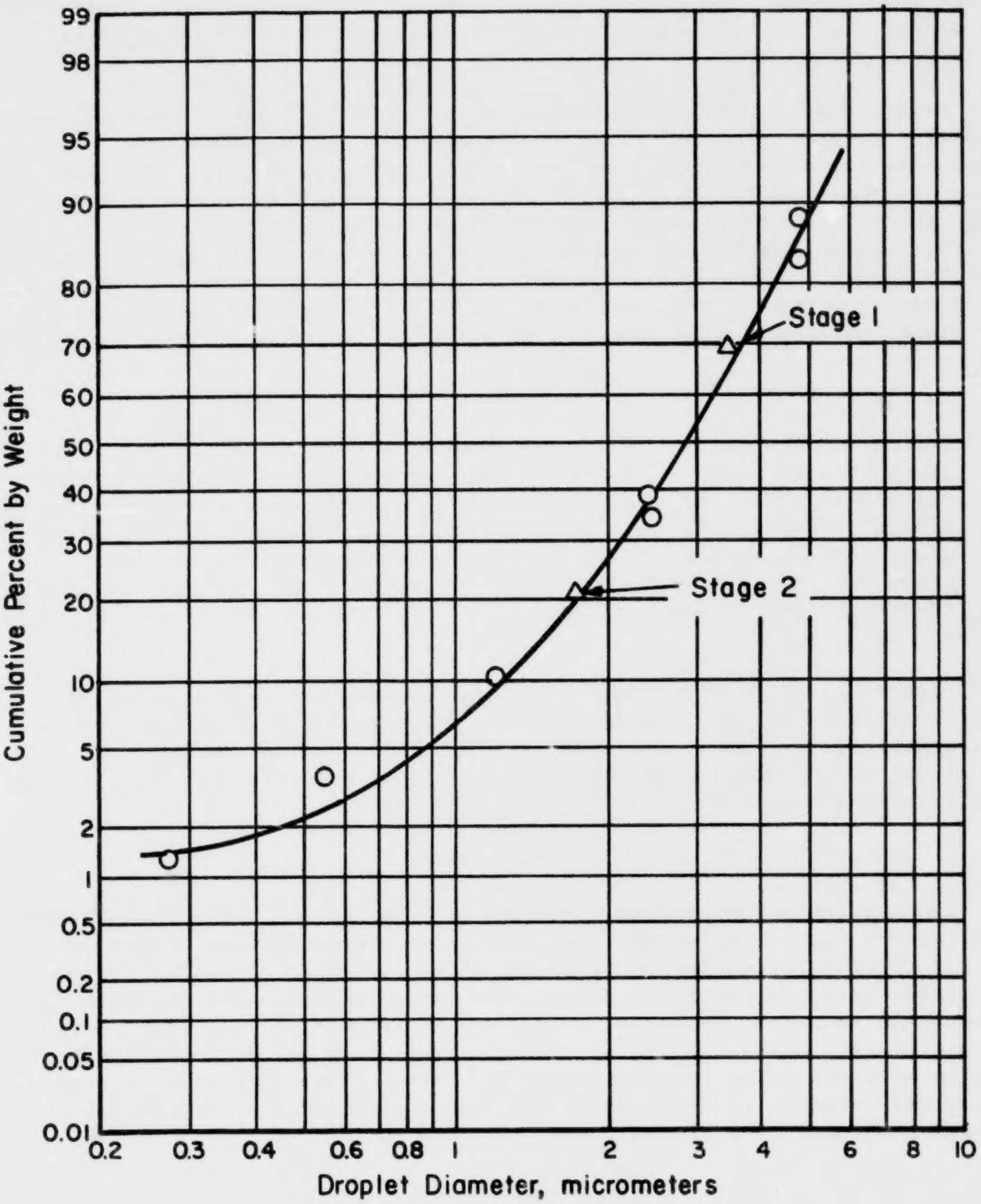

Figure 6. Particle size distribution data of fluorescent aerosol package - Can "E".

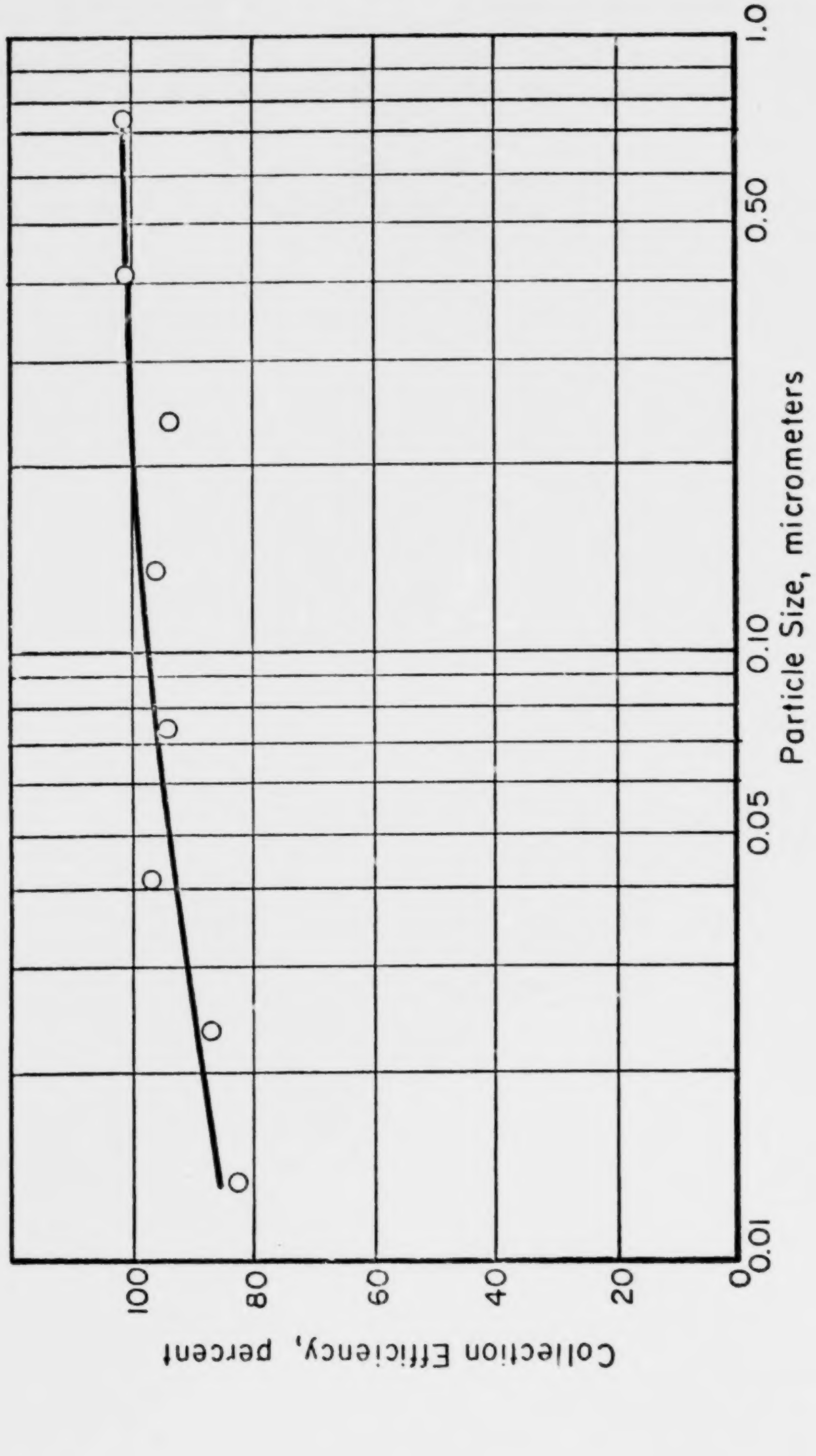

Figure 7. Collection efficiency of Mark II massive-volume sampler obtained with the Minnesota aerosol analyzing system on ambient particles.

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COMPOUND IDENTIFICATION OF LOS ANGELES CATALYST STUDY SAMPLES

Edward P. Parry and Leo E. Topol

Rockwell International
Newbury Park, California

M.D. Lind, A.B. Harker, and R. M. Housley
Rockwell International
Thousand Oaks, California

and

Franz J. Burmann

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

With the use of a Battelle massive sampler, discrete samples have been collected at two sites, upwind and downwind of the San Diego Freeway. These samples have been analyzed by X-ray diffraction, X-ray emission spectroscopy using a scanning electron microscope, photoelectron spectroscopy, and wet chemistry. The Battelle sampler separates the samples into three size fractions, the first two separations being by impaction and the final separation by an electrostatic precipitator. Material from all three stages has been analyzed. The electrostatic precipitator samples have also been compared with Teflon filter samples prepared simultaneously. In addition, laboratory-generated aerosols were prepared to evaluate their behavior as a function of temperature in the photoelectron spectrometer and their detectability by X-ray diffraction. Several sulfates have been identified in the Battelle samples. In addition, artifact formation in the Battelle sampler has been noted for long-term samples. The results are presented and discussed.

INTRODUCTION

The Los Angeles Catalyst Study (LACS) is a program designed to determine possible increases in sulfate levels as a result of automobiles equipped with catalytic converters. Since the effect of sulfate on health varies with the individual sulfate compound, the identification of the specific sulfate species in particulate samples collected in areas of heavy automobile traffic is desired.

Some preliminary work has been done on samples collected with a Battelle massive sampler using various analytical techniques. While lead sulfate was present, no specific ammonium compounds could be identified in the collected particulate. Results also strongly suggested that artifact formation was occurring in the Battelle sampler. Some experiments have been done in an attempt to define this.

In this paper, the nature and limitations of the techniques used will be discussed and a potentially useful technique to infer compound information using photoelectron spectroscopy will be described. Finally, some of the preliminary results will be discussed.

TECHNIQUES - NATURE AND LIMITATIONS

The techniques which have been employed in this study and some brief comments about them are given below and are summarized in Table I.

X-RAY DIFFRACTION (XRD)

X-ray diffraction, employing Debye-Scherrer powder patterns, was used to identify the crystalline components of aerosols. Amorphous substances do not yield XRD lines. The aerosol sample can be examined directly on the filter substrate or can be separated from the collector and packed into a glass capillary. The use of the filter has the obvious advantage of minimizing handling and artifact formation but it has two problems. First, the Teflon filters generally used yield XRD lines, which complicate the analysis. Second the amount of sample exposed to the x-ray beam may be too low to produce detectable lines. We have found that about 10 μg/cm^2 of $(NH_4)_2SO_4$ will give strong, well-defined diffraction lines. Increased detectability of crystalline aerosols collected on a filter can be obtained either by folding the filter several times so that the x-ray beam penetrates more layers of sample, or by separating the deposit from the filter which concentrates the sample to a smaller volume. This separation can be accomplished by dissolving away the filter, but one must be careful that the sample is not altered in the process. In addition to the problem of decreasing intensity of the line with the quantity of compound present, the lines broaden as the crystallites become small. The crystallite size, where line broadening commences, will vary with each compound and must be determined but, generally, is around 0.03-0.1 μm. Thus, for nucleation mode particles, which are about 0.04 μm and are expected to be present in high concentration near sources such as a freeway, XRD may not be amenable. However, this must be determined. If nucleation mode particles of ammonium nitrate and sulfate do not yield identifiable XRD patterns, then the technique is limited to the accumulation mode size particles or recrystallized material.

Although XRD is one of the few tools available to us that give direct evidence as to the identity of a component, the analysis is complicated since aerosols are composed of numerous constituents and the XRD patterns are quite complex. To simplify this task, elemental analysis is utilized. Another technique, fractionation of the mixture with solvents specific to certain sulfates can be used to simplify the diffraction patterns. The negligible formation of artifacts in this fractionation process must be established.

TABLE I. TECHNIQUES AND PERTINENT INFORMATION

Technique	Sample Required	Limitations	Information Obtained
X-Ray Diffraction (XRD)	10-50 $\mu gm/cm^2$ On filter or without substrate	For crystals of $\gtrsim$ 0.1 μm size. Mixture of many compounds yeild complex pattern.	Identification of compound in bulk sample.
X-Ray Photoelectron Spectroscopy (XPS)	5 $\mu gm/cm^2$	For surface analysis (10-40Å), clean substrate stable over wide temperature range (non-backed Teflon).	Identification of Element (except H) and oxidation state; from temperature behavior can get indication of volatile sulfates, nitrates, etc.
Scanning Electron Microscope with EDAX	1-5 $\mu gm/cm^2$	For analysis (to 0.5 μm), elements heavier than Na.	Elemental analysis of specific crystals.
Wet Chemistry (Inorganic)	1 $\mu gm/cm^2$ *		Qualitative amounts of bulk species.
Wet Chemistry (Organic)	10 m gms/cm^2		Acid, base and neutrals; aliphatic, aromatic and oxygenated fractions.

* Extracted into 10 ml H_2O.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS or ESCA)

XPS measures the kinetic energies of photoelectrons expelled from a sample irradiated with monoenergetic x-rays. The spectrometer measures the intensity of the electrons emitted as a function of their kinetic energy. The electron binding energies are characteristic for each element and so enable the method to be used for elemental analysis. The binding energies for an element are modified by the valence electron distribution, i.e. oxidation state. In general, atoms of higher oxidation states have higher binding energies with respect to the neutral atom (positive chemical shift), and for reduced states they will show a negative shift. The XPS technique can, therefore, be used for both elemental analysis (for elements heavier than He) and for determination of oxidation state. The relative amounts of the elements can be obtained from the spectral amplitudes. However, to obtain quantitative results, an element in the sample must be analyzed by another technique. Since XPS analyzes only a 10-40A depth of the exposed particles, the surface concentrations are obtained and these may not be similar to bulk concentrations.

Since the technique is a surface tool, particulates imbedded in the filter matrix will not be analyzed. Teflon filters are, therefore, the best substrates. Fiber glass cannot be used because of the uneven nature of the surface and the impurities in the filter. Sample concentrations of about 5 $\mu g/cm^2$ are sufficient for analysis, and as with XRD the response signal can be better defined with longer exposure times.

Although XPS does not identify compounds directly, such information can be gathered by observing the temperature of volatilization of the species present. For this, a means of varying the temperature of the sample from -150° to +250° is used. Sulfuric acid will volatilize rapidly in the vacuum of the XPS spectrometer (10^{-8} Torr) at about 0°C and can be determined by the disappearance of the S(VI) peak. NH_4NO_3 will also start to volatilize at about 0°C and both the +5 and -3 nitrogen spectra will decrease. The ammonium sulfates are more stable and will persist to temperatures well over 100°C. For these thermal measurements, unbacked Teflon filters can be used up to 250°C.

SCANNING ELECTRON MICROSCOPE (SEM)

The SEM utilizes a well-focused electron beam to scan over the target sample. Secondary electrons emitted from the sample yield its image and topography on a screen. Sample areas of 100A (.01 μm) can be resolved and samples of a few $\mu gm/cm^2$ are required. The surface of the sample must be conducting which can be readily accomplished, if necessary, by covering the sample with a conducting material such as graphite, aluminum or gold. The SEM is used to obtain morphological information which helps determine if artifact formation has occurred, e.g. recrystallization to large crystals, crusting, etc. Samples can be examined on a filter substrate or in special containers. Since the SEM is also run under vacuum, a cold stage is available for volatile samples.

The SEM, used in the present studies, also has an "energy dispersive analysis by x-ray fluorescence" (EDAX) capability. In addition to the secondary electron beam, x-rays, characteristic for the various elements are also emitted from the sample. This method permits analysis of elements heavier than sodium. This analysis is qualitative for large areas, but is more definitive for single particles especially if standards for the elements of interest are available. The depth of penetration is about 0.5 μm since self-absorption of the x-rays occurs.

WET CHEMISTRY

The methods used on standard LACS samples have been employed in this study for analysis of NH_4^+, $SO_4^=$ and NO_3^-.

ORGANIC ANALYSES

For organic analyses, the method of Hoffman and Wynder (1) is being tested. About 100 mg of sample is required and the organic particulates are separated from the rest of the sample by extraction in ether. The ether is mixed with 2N H_2SO_4 which removes the basic fraction. The ether layer is then extracted with 2N NaOH which removes the acid fraction. The neutral organics remain in the ether. The neutral portion can be fractionated into aliphatic, aromatic and oxygenated fractions by column chromatography with n-hexane, n-hexane + benzene, and ether, respectively.

USE OF XPS AND XRD TO INFER NATURE OF COMPOUNDS

In the preceding section a technique to infer compound structure from XPS data at different temperatures was briefly described. By obtaining XPS spectra of pure compounds as aerosols on filters at different temperatures and determining the relative decrease of the individual species with temperature, useful information can be obtained about volatilization ratios of various ions. From this information, inference can be made about the compounds in the sample. For example, Figure 1 shows the temperature behavior of a synthetic sample prepared by collecting on a filter sulfuric acid aerosol generated by using a Baird Atomic generator. The size distribution was measured with a Thermo-Systems Electrical Aerosol Analyzer.

The increase in signal between about -40° and 0° is probably caused by evaporation of other volatile material from the surface, thus exposing more sulfate. The decrease between 0° and about 30° is the result of the loss of sulfuric acid while the gradual decrease beyond this point is probably the decrease caused by some ammonium bisulfate contamination in the sample caused by air exposure.

The volatilization temperature ranges for the various synthetic aerosol compounds commonly expected in ambient particulate are shown in Table II.

In addition to the XPS work, filters of synthetic aerosol samples were examined by x-ray diffraction to determine how concentration of submicron size (0.075 - 0.1 μm) aerosols affect the x-ray diffraction pattern. The lowest concentration of aerosols that yield an identifiable XRD pattern with 12-hour exposure, and the corresponding ambient concentrations required to yield such samples with 2-hour sampling time at 100 l/min on 47 mm Fluoropore filters are shown in Table III. For the ambient aerosols, the assumption was made

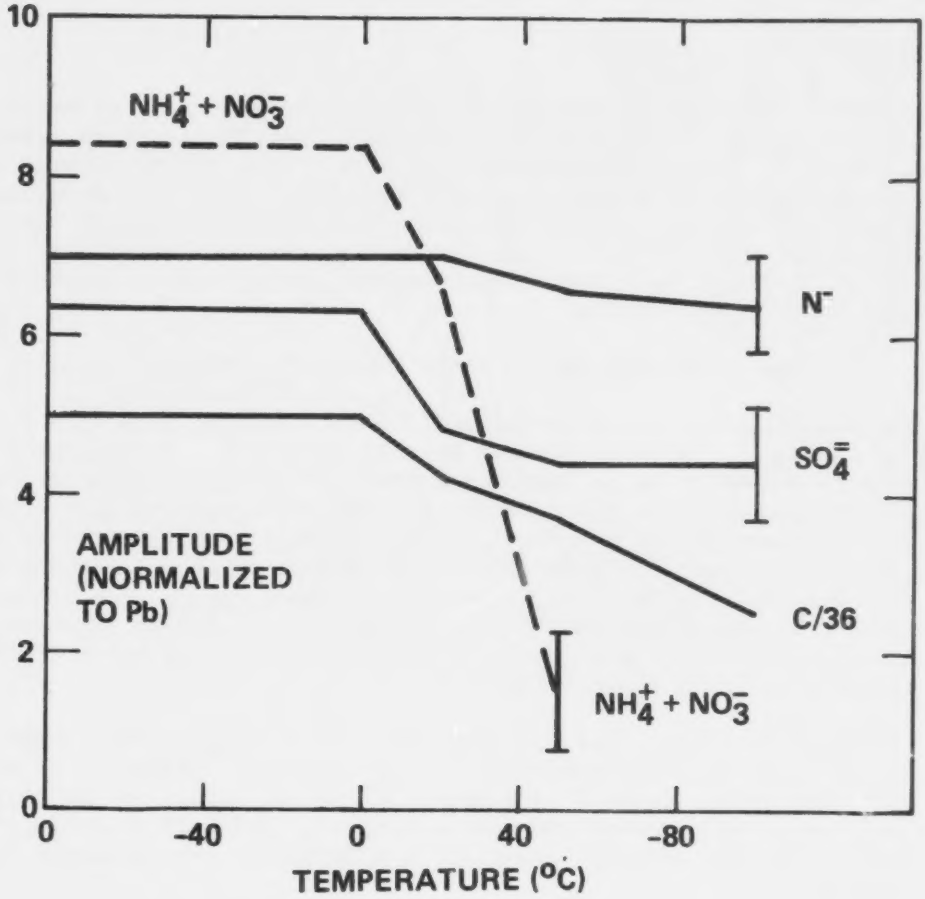

Figure 1. XPS of ambient aerosol (electrostatic precipitator).

TABLE II. VOLATILIZATION TEMPERATURE RANGE OF AEROSOL COMPOUNDS IN XPS SPECTROMETER
(10^{-8} torr. vacuum)

Aerosol	Temp. Range Studied ($T^{\circ}C$)	Volatilization Temperature Range	
		Initial ($T^{\circ}C$)	Final ($T^{\circ}C$)
H_2SO_4	-90 to +40	0	(20) *
$(NH_4)_2SO_4$	-130 to +200	30	200
NH_4HSO_4	-60 to +100	0	(200) *
NH_4NO_3	-130 to +110	0	100
NH_4Cl	-90 to 100	50	(120) *

* Estimated

TABLE III. DETECTION LIMIT OF SUBMICRON AEROSOL BY XRD

Aerosol	Quantity Seen ($\mu g/cm^2$)	Ambient Concentration * ($\mu g/m^3$)
$(NH_4)_2SO_4$	11	10
NH_4HSO_4	> 50	> 40
$NH_4HSO \cdot (NH_4)_2SO_4$	50	40
NH_4NO_3	> 50	> 40
NH_4Cl	> 50	> 40
$(NH_4)_2SO_4 \cdot 2NH_4NO_3$	Does not form readily	
$(NH_4)_2SO_4 \cdot 3NH_4NO_3$	Does not form readily	

* For two-hour sampling at 100 l/min with 47 mm filter.

*TABLE IV. ANALYSIS OF LACS SAMPLES **

Impactor Dust			Electrostatic Precipitator Dust		
Both Sites			Both Sites		
EDAX(4)	ESCA(2)	XRD(1)	EDAX(4)	ESCA	XRD
Mg	Fe	$Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (3)	Al	N (amine- and/or amide-types at -25 to 25°C), (Ammonium and nitrate at -25°C only)	
S	N	SiO_2	Si	C	Many well-defined
Al	S (87% $SO_4^=$)	no $PbSO_4$	S	S (86% $SO_4^=$) (14% S or $S^=$)	lines obtained.
			Ca		Patterns similar
Si	C		Cl	Pb	for both sites.
K			Fe		
Ca			K		$PbSO_4$ both sites
Fe			Pb		
			Br		

* Samples collected with a Battelle Sampler
(1) Samples from both stages and both Sites A and C gave similar results
(2) Analysis of the small particles of second stage of Site C
(3) Analysis of a single large (100 μm) crystal particle from second impactor stage from Site C
(4) Energy dispersive analysis by X-ray fluorescence (with scanning electron microscope)

that presence of other ions does not decrease the sensitivity of XRD. The detection limits given in Table III were determined with unfolded filters. However, the sensitivity of the XRD technique has been improved considerably by folding the filter sample several times, thus resulting in exposure of multilayers of sample to the x-ray beam. With this technique, 10.8 μg/cm^2 of $(NH_4)_2SO_4$ were recently analyzed in a 4-hour exposure versus over 12 hours for a single filter layer. The synthetic aerosols used in these experiments consisted primarily of 0.075 μm particles but scanning electron micrographs showed particles of up to 1 μm size and a non-uniform distribution on the filter.

ARTIFACT FORMATION IN SAMPLE COLLECTION

In the original studies (2), composite samples, collected with the Battelle massive sampler, were used. Results suggested that possible changes occurred in the sample during and/or after collection as determined by crystal growth and bulk caking of the sample. These changes could arise by (1) water condensation on the sample with subsequent dissolution, reaction and recrystallization; (2) reaction of particulates with the sampler collector surface; (3) reaction of collected particulates with reactive gases; and (4) reaction between individual particles.

Some preliminary experiments have been done in which various sample collection conditions have been used. Results of scanning electron micrographs and chemical analysis obtained from samples collected on the electrostatic precipitator plates have been compared with samples collected on Teflon filters. Differences have been found but to date the exact causes for the differences have not been identified.

In order to obtain the filter sample as described just above, an opening in the side of the Battelle sampler, below the impactor stages, was made. A sample was drawn from this opening, through a Teflon filter at about 100 l/min. Thus, both the filter and the electrostatic precipitator plates were sampling the same material. Some comparison of the precipitator samples has also been done with samples collected using a dichotomous sampler. The small amount of particulate on 4-hour dichotomous filters makes the use of the XRD and XPS techniques rather difficult.

The use of the Battelle massive sampler requires that the particulate fraction collected on the precipitator plates undergo significant handling before a sample is ready for analysis. For most analytical techniques employed, particulate samples collected on Teflon or membrane filters can be used directly. For this reason, direct collection of samples on filters has an advantage. However, a longer collection time is required to obtain sufficient sample if a dichotomous sampler is used.

AMBIENT SAMPLE ANALYSES

During the early part of the program, Battelle samplers were operated continuously at sites A and C and the material collected was scraped off and composited. Preliminary work was done with approximately a six month composited sample. Results are summarized in Table IV.

All the x-ray diffraction patterns contained numerous well-defined lines indicating the presence of crystalline compounds. Samples from all the impactor stages resulted in similar patterns, but these patterns differed substantially from those of the electrostatic precipitator. Large single crystals ($\sim$ 100 μm) of $Mg\ (NH_4)_2(SO_4)_2 \cdot 6H_2O$ have been found in all the impactor samples, indicating crystal growth after particle size separation. In addition, the sample material was caked and crusted, indicating that compound identification with this sample and possibly with this collection device may not be representative of the compounds in the air.

Ammonium sulfate has not been identified in any of the samples, but lead sulfate was found in both precipitator samples. Further, both precipitator samples contained large amounts of sulfur and a significantly larger quantity of lead was present at site C than A. About 86% of the sulfur is present as sulfate with the remainder in the elemental or reduced form. About one-third of the sulfate observed by XPS is volatile at temperatures slightly above ambient in the vacuum of the XPS instrument. In addition to the sulfur and lead, the chief elements present in the precipitator samples are Al, Si, Cl, K, Ca and Fe. None of the common sulfates of these cations has been identified by XRD. XPS measurements showed the presence of NH_4^+, NO_3^- and amine or amide species at -25°C, but at room temperature the NH_4^+ and NO_3^- had volatilized completely in the vacuum of the XPS spectrometer. Significant concentrations of organic matter were also present in the precipitator samples.

The Battelle sampler has more recently been operated at the peak period (3:00 to 7:00 pm) for two successive days at site A. About 250 mgs of sample was obtained from the precipitator plates, and this was approximately 88% of the total material recovered from the sampler.

Photoelectron spectroscopy was used to obtain spectra at various temperatures to suggest possible compounds present. Figure 2 shows the behavior of the XPS signal as a function of temperature for the various species of interest. The intensities are ratioed to lead. Of most interest, perhaps, is the fact that only about 29% of the surface sulfate is volatile at 100°C in the vacuum of the spectrometer (10^{-8} Torr). This might suggest that the majority of sulfate is in various forms of non-volatile compounds (e.g. Na_2SO_4, etc.). However, the temperature was not taken high enough to rule out the presence of a small amount of ammonium sulfate. Because the nitrate and ammonium peaks decrease together, it suggests that the majority of the ammonium ion is in the form of ammonium nitrate.

The x-ray diffraction pattern did not show lines for lead sulfate or for ammonium sulfate. However, it must be remembered that the technique can be limited by the size of the particulate and the amount of sample present.

High-volume filter samples have been extracted with ether and about 50% of the sample was dissolved. Using the scheme of Hoffman and Wynder (1) for one sample, the percentage of total organic and acidic, basic and neutral fractions is given in Table V.

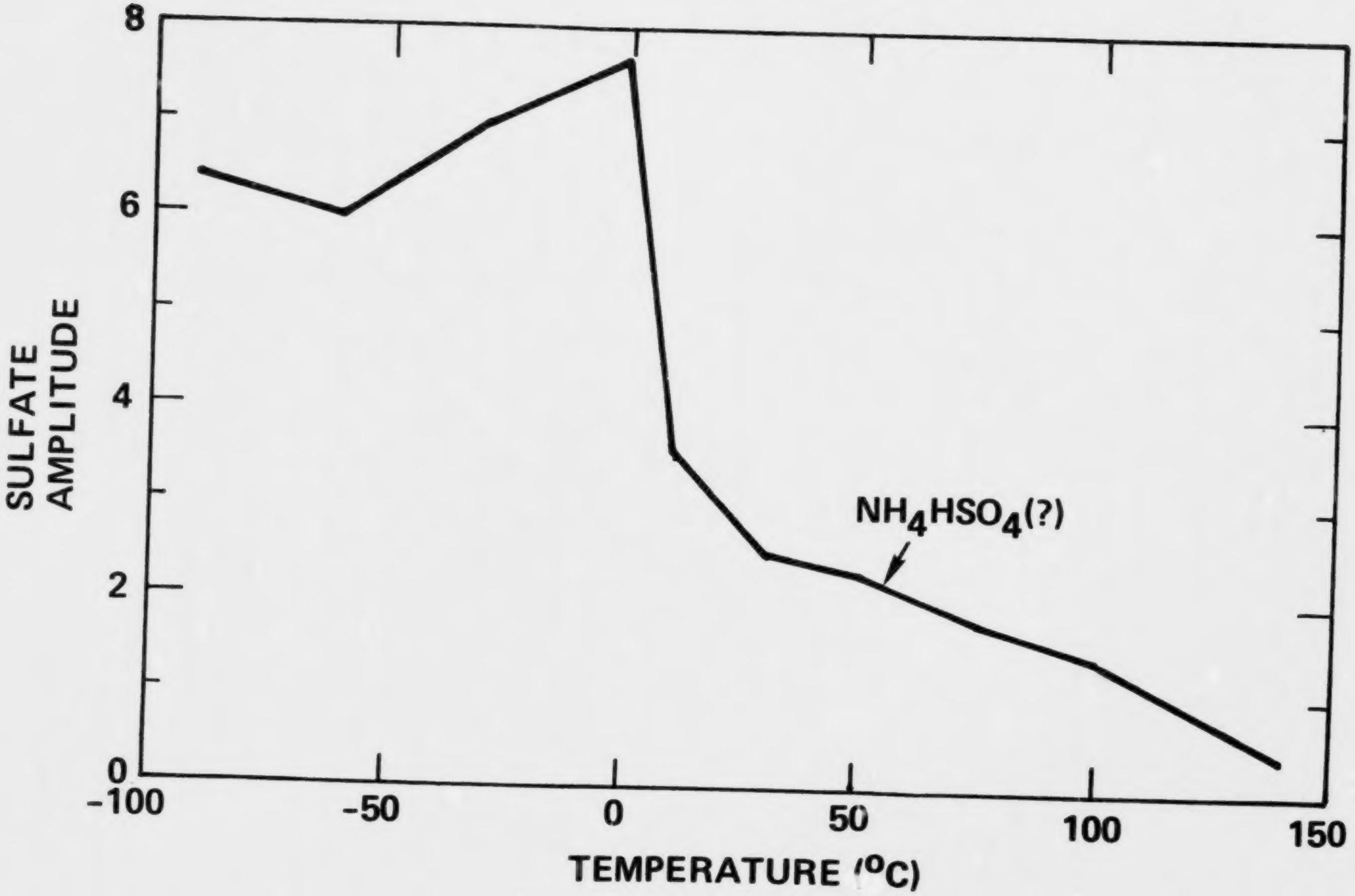

Figure 2. XPS for H_2SO_4 aerosol.

TABLE V. ORGANIC PARTICULATE ANALYSES

Fraction	Weight % of Total Sample
Total Organics	57.3
Basic	Negligible
Acidic	28
Neutral	18.6
Insoluble	10.7

CONCLUSION

In summary, samples collected from the precipitator plates (and from side stream filters) of the Battelle sampler after 8-hours of operation appear caked and contain large particles. The use of a dichotomous sampler does not produce a large enough loading in a 4-hour period for XRD or XPS. A technique has been described in which the nature of compounds present in a sample can be inferred by x-ray photoelectron spectroscopy. Synthetic aerosols have been generated and used to verify and calibrate the technique. Preliminary work on ambient samples suggests a significant amount of sulfate is non-volatile. In some samples, lead sulfate has been identified by x-ray diffraction. Preliminary work suggests that a significant amount of the freeway aerosol sample may be organic.

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2. "Preliminary Report - Compound Identification of LACS Samples (Los Angeles Catalyst Study)", prepared by Rockwell International Air Monitoring Center for Environmental Protection Agency, August 1976.

COMPARISON OF LEAD RECOVERY WITH AND WITHOUT THE USE OF A LOW TEMPERATURE ASHER BEFORE EXTRACTION

Lloyd S. Shepard and April Price

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

Results of Pb^{++} analysis with and without the use of a low temperature asher are presented. Comparable results can be obtained by these two sample preparation methods although indication of slight losses during the low temperature ashing step occur.

INTRODUCTION

The conventional method of trace metal analysis in particulates involves nitric acid extraction followed by atomic absorption (AA) determination of the metal(s) of interest. This method is effective provided that the particles containing metallic compounds are not covered with carbon containing substances such as soot, oils and/or other organic compounds which may decrease the efficiency of the acid extraction. This problem can be overcome easily by prior ashing of these samples with a low temperature asher, which is proven to eliminate possible losses of volatile metals (i.E. Hg, Zn, Cd, Pb) which do take place with conventional muffle furnace ashing. At the early stages of the Los Angeles Catalyst Study (LACS), an effort was made to determine if application of low temperature ashing is necessary in the analysis of particulate lead (Pb) collected close to the San Diego Freeway by means of high volume samplers.

EXPERIMENTAL PROCEDURE

Duplicate strips of high-volume samples collected at the LACS sites were analyzed for Pb with and without the use of low temperature asher with the following procedure. The first strip was ashed at low RF energy and with oxygen passing over the sample at a low rate (4 cc/min) for approximately 10 minutes or until ashing was complete. The strips were than transferred to acid-washed 50-ml beakers and the ashing boat rinsed with a few ml HNO_3

(1:10 diluted) to remove any dislodged particles. The samples were then boiled for 20 minutes, filtered and diluted to 24 ml for four hour samples or to 100 ml for 24 hour samples.

The treatment of the second strip was identical as above with the omission of the ashing step.

The solutions thus obtained were analyzed for Pb by atomic absorption by employing a 303 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Twenty-six duplicate strips of exposed filters from the LACS project were analyzed with and without prior ashing by the low temperature asher according to the procedures described above. Ten of the duplicate strips were 24 hour integrated samples and the remaining 16 were four hour integrated samples.

Table I lists the results of the analysis of the duplicate samples. The average range of the duplicate analysis with and without ashing is 0.20 μg/ml with an upper control limit of 0.65 μg/ml. These compare very well with the previously established operational control limits for analysis of duplicate lead samples, 0.28 μg/ml and 0.91 μg/ml, respectively. Only one value (sample No. 8) is out of control. The average percent difference with the exception of four samples, very low in Pb (sample Nos. 14, 16, 17 and 20), is 3.1 with a standard deviation ± 2.8 which is not very uncommon with this type of sample.

The comparison of the results with and without ashing is also presented in Figure 1. The correlation coefficient was found to be 0.998 and the slope and intercept of the least squares fit were 0.972 and 0.058, respectively. The slight deviation of the slope from unity may suggest a loss of Pb during the ashing step. Statistically, however, the results obtained with or without the use of the low temperature asher should be considered equivalent. These results clearly show that low temperature ashing is not necessary for the atomic absorption determination of Pb in the LACS samples.

TABLE I. DUPLICATE LEAD ANALYSIS WITH OR WITHOUT LTA

SAMPLE NO.	SAMPLING TIME (hr)	NOT ASHED μg/m1	ASHED μg/m1	% DIFF.*
1	24	5.18	4.93	-4.94
2	24	5.18	5.12	-1.16
3	24	7.34	7.34	0.00
4	24	9.34	9.14	-2.16
5	24	4.68	4.93	5.20
6	24	7.02	6.92	-1.43
7	24	8.50	8.00	-6.06
8	24	11.77	10.89	-7.77
9	24	5.28	4.96	-6.25
10	24	5.92	5.79	-2.22
11	4	0.69	0.69	0.00
12	4	12.33	12.58	2.01
13	4	12.59	12.08	-4.13
14	4	0.32	0.20	-46.15
15	4	12.68	12.11	-4.60
16	4	0.79	0.97	20.45
17	4	0.50	0.42	-17.39
18	4	1.64	1.49	-9.58
19	4	4.05	4.00	-1.24
20	4	0.34	0.40	16.22
21	4	8.60	8.54	-0.70
22	4	12.85	12.77	-0.62
23	4	9.48	9.34	-1.53
24	4	9.52	9.52	0.00
25	4	4.21	4.46	5.77
26	4	5.76	5.79	0.52

$$* \text{ \% DIFF.} = \frac{\text{ASHED} - \text{NOT ASHED}}{\text{AVERAGE}}$$

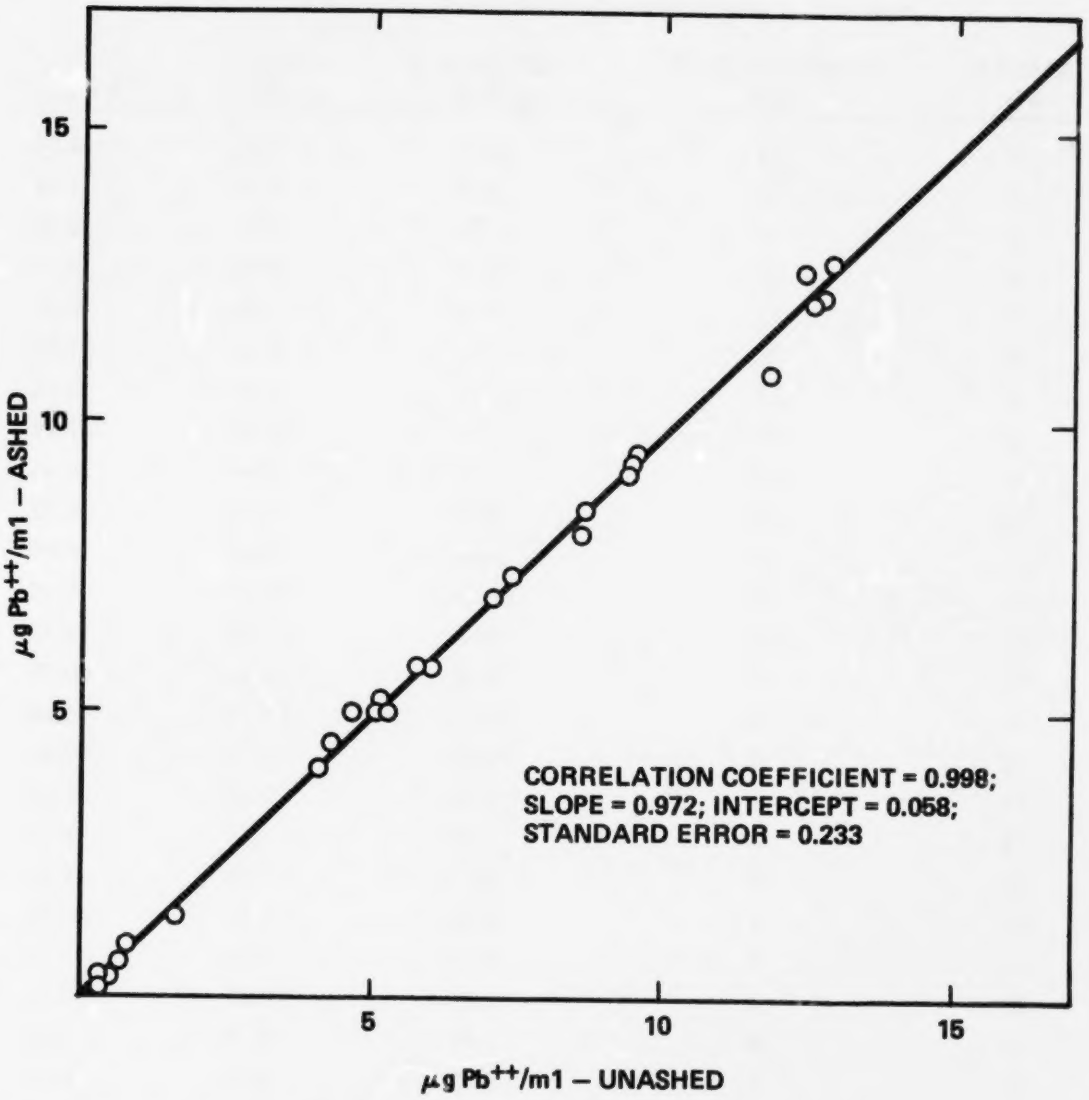

Figure 1. Comparison of lead recovery with and without the use of a low temperature asher before extraction.

TABLE I. DUPLICATE LEAD ANALYSIS WITH OR WITHOUT LTA

Sample No.	Sampling Time (hours)	Not Ashed µg/ml	Ashed µg/ml	% Diff. *
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26	4	5.76	5.79	0.52

$$* \; \% \text{ Diff.} = \frac{\text{Ashed} - \text{Not Ashed}}{\text{Average}}$$

DETERMINATION OF PERCENTAGE OF DIESEL TRUCKS AND CATALYST EQUIPPED CARS

Edward P. Parry and Raymond A. Meyer

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The percentage of catalyst equipped cars passing the study site is a critical parameter. Several techniques to obtain this information, such as infrared surveillance, passing vehicle identification, etc., were considered. The infrared surveillance required considerable research, and there were no available personnel capable of vehicle identification. Los Angeles County new car registrations have been studied since September 1974 to determine the percent of catalyst equipped automobiles within the county. The monthly increase rate, 0.5%, has been quite constant over the period. These data alone do not establish the catalyst equipped car ratio at the freeway study site and must be modified by a use factor. This factor is presently under investigation. Diesel truck exhaust contains a high sulfate level which could perturb the data. Therefore, a diesel truck count was made for 15 consecutive days in September 1976. Truck movement was determined by the hour and direction. Data are reported for 13 days, during which trucks were counted from 0800 - 1200 and 1500 - 1900, and two days, which were counted for 24 hours. Both weekdays and weekends were included in the study.

INTRODUCTION

The number of cars which are equipped with the catalytic converter is an obvious parameter which must be known in order to project the impact of sulfate emission from these cars on ambient sulfate levels. Beginning with 1975 models, it was mandatory in California to have the catalytic converter on automobiles from most manufacturers in order to meet California emission standards. Thus, 1975 and later models of most makes of automobiles were equipped with the catalytic converter, while 1974 and earlier models were not. In the initial stages of the Los Angeles Catalyst Study (LACS), an investigation was undertaken to evaluate various techniques which could be used to determine the number of vehicles passing the LACS site which were equipped with the catalytic converter.

Another source of freeway particulate sulfate is diesel trucks. The exhaust of diesel trucks is reported to contain a rather large concentration of sulfate, and the sulfate emission per mile is very large. In order to determine the potential contribution of these trucks to freeway sulfate levels, a rather recent determination of the number of diesel trucks passing the LACS site has been made.

In this paper, the approaches which were investigated, those finally selected and the results of the determination of both diesel trucks and cars equipped with catalytic converters are discussed. In addition, improvements in the method to determine the percentage of catalyst equipped cars are discussed.

DIESEL TRUCK STUDY

With a little experience, identification of diesel trucks by visual observation is straightforward. In this study, college students were employed to count the diesel trucks as they passed the site. Small hand held counters were used, and the personnel were stationed at the side of the freeway at the LACS site. The study was divided into two phases. In the first phase, trucks were counted during the two peak periods, 0800-1200 and 1500-1900, from Monday, 13 September 1976 through Sunday, 26 September 1976. In the second phase, trucks were counted for two 24-hour periods, one on Sunday, 3 October 1976 and the other on Thursday, 7 October 1976. These periods were chosen to study all types of traffic flow. In Figure 1 a bar graph is presented showing the distribution of northbound and southbound traffic for the peak periods over the two week time span of this study. In general, there is significantly more traffic in the 0800-1200 time period. The total trucks for the two peak periods is, in nearly every instance, somewhat less than 1000. In Figure 2, the diurnal traffic pattern is shown for the two 24-hour periods. From about 0600 in the morning until 1800 at night, on weekdays, a sawtooth pattern is found with traffic density above 50 trucks per hour. Sunday truck traffic is small as would be expected. The total 24-hour truck count for both northbound and southbound for the Thursday period was 2,252. The total number of vehicles for the same period (both north and southbound) was approximately 175,000 cars. The truck traffic thus amounts to about 1 to 2% of the total traffic.

APPROACH TO DETERMINE THE NUMBER OF CATALYST EQUIPPED CARS

Several different approaches were initially proposed. These included the use of time-lapse photography, thermal imagery, methods to mark 1975 cars uniquely at the time of registration for later identification, car registration information and others. Some of these techniques were shown not to be feasible, as preliminary evaluation and investigation of the techniques uncovered very difficult problems (e.g. unique tagging of 1975 vehicles). Some of the other approaches were considered in a little more detail. These are described below:

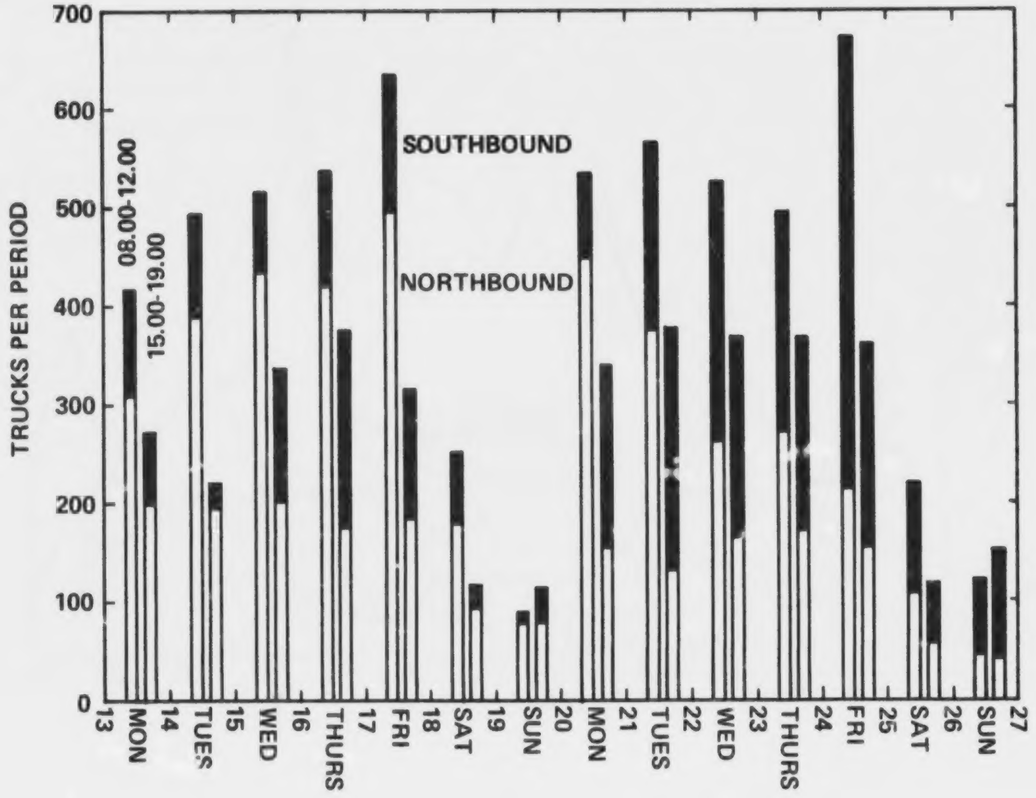

Figure 1. Diesel truck peak period study.

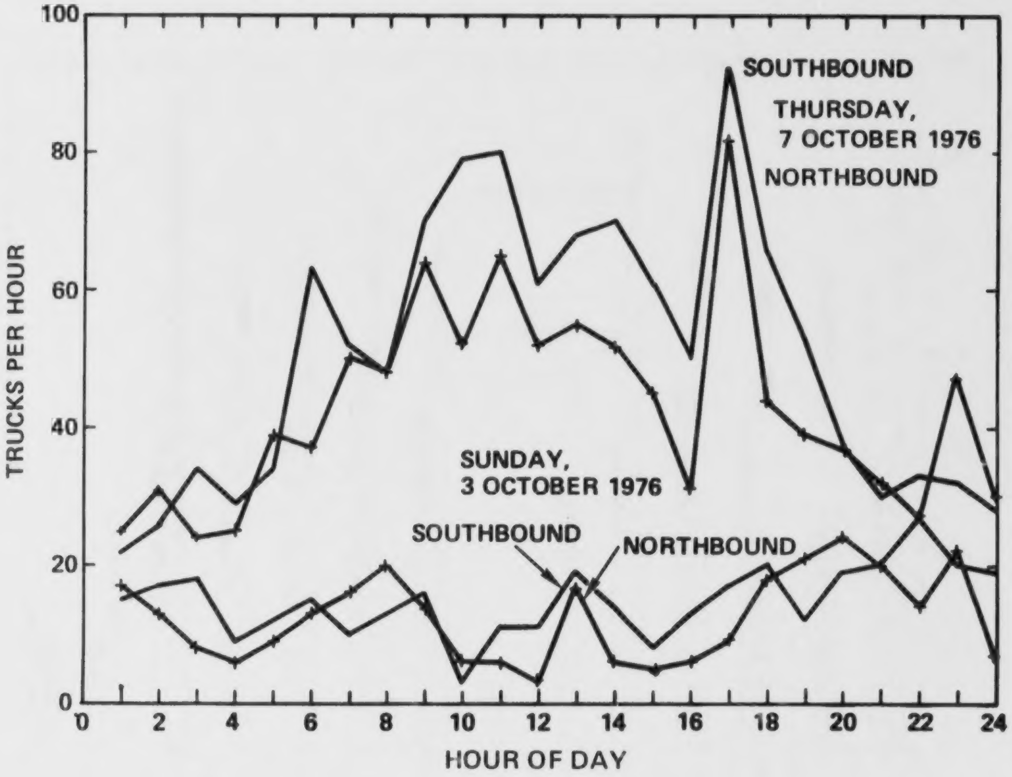

Figure 2. Twenty-four hour truck count.

THERMAL IMAGERY

Catalytic converters increase the temperature of the exhaust gas by a significant amount. The use of thermal imagery to scan the tail pipe temperature of passing automobiles remotely was considered. Systems for this purpose are available commercially. A disadvantage of the system is cost. A question also exists with regard to the resolution of the system since there is some variation in operating temperature of catalytic converters, and in muffler and tail pipe designs which will cause variations of the temperature of the exiting gas from various car makes. Another question concerned the possibility of measuring tail pipe temperatures for cars in all traffic lanes, especially in heavy traffic, without interference from surrounding cars. A third question which had to be answered before the technique could be used involved the ability to differentiate exhaust pipe heat sources from others including reflected infrared energy, engine heat sources and others.

This technique has the advantage that it identifies catalytic converter equipped cars directly and without assumptions. The disadvantage is that the perfection of the technique would take considerable research and development and the cost of equipment is rather high. Further work was not carried out with this technique.

VISUAL RECOGNITION OF MODEL YEAR

Some years ago it was possible to recognize the model year of practically every car on the road by the distinguishing characteristics introduced by the manufacturer with each new model year. This could form the basis for differentiating 1975 model cars from older ones and, thus, indirectly getting the number of cars equipped with the catalytic converter. Two approaches could be considered in this proposed method. One would be real-time identification by having people stand on the side of the freeway, or on an overpass near the LACS site, and physically count the cars of interest. Another approach which has obvious advantages is to use time-lapse photography to photograph a statistical sample of automobiles as they pass the site and perform the identification at a later date. A valid statistical sample is obviously a necessity. If the photographs were good, the ability to study cars as required in order to identify small differences between models is an advantage. In addition, the photographs form a permanent record which could be used for later verification and checking as necessary. The time-lapse photographic approach has some obvious advantages in obtaining good photographs of cars in all traffic lanes (particularly at night) and in obtaining assurance that a valid statistical sample is being used.

The determination of make and model year of present automobiles is not trivial. Although it might have been a casual observation, it appeared to us as if model year distinction of various makes of automobiles has become more difficult in recent years because only very minor changes are being made to the exterior for succeeding model years. To determine how diffcult this distinction might be, inquiries were made of various private and public agencies. The list included: California State Highway Patrol, Los Angeles City Police Department (both Traffic and Auto Theft Divisions), the Automobile Club of Southern California (AAA), editors of several automobile publications, such as Road and Track, several automobile retailers and used car outlets, zone offices of major automobile manufacturers, etc. All of the people contacted stressed the fact that during the past few years external changes between model years were very subtle and in some cases non-existent. These contacts have indicated that an effort directed toward visual identification of traffic passing the site would not be successful. Because of the difficulties uncovered in the assessment of this approach, no further work was done.

LEADED-UNLEADED GASOLINE SALES

All catalyst equipped cars are required to use unleaded gasoline. Because unleaded gasoline is more expensive, it might not be too unreasonable to assume that drivers of non-catalyst equipped cars will, in general, not use unleaded gasoline. If, in addition, it is assumed that the overall gasoline mileage of the mix of 1975 and later models is about the same as the pre-1975 models, the use of gasoline sales might be an approach to determine the percentage of catalyst equipped cars. However, the difficulty of validating the assumptions required and the fact that this approach does not give percentage of catalyst cars passing the LACS site makes it questionable. No further work was, therefore, done.

REGISTRATION DATA

During the early stages of the LACS program, an approach was proposed in which the license plates of automobiles passing the site would be photographed and the model year subsequently identified by checking the plate against state registration data. This approach needed a research and development effort in order to develop techniques to obtain legible photographs of license plates of cars in all lanes of the freeway, especially at night during heavy traffic. In addition the State Department of Motor Vehicles (DMV) charges $1.75 to identify make and model year from each complete license plate number. The cost of this program thus seemed prohibitive and was, therefore, not carried further.

New car registration information was next considered. For a very nominal charge, the State Department of Motor Vehicles will provide a monthly summary of car registrations. In addition, several private companies buy the registration information from the state, reduce the data, and sell reports of interest to automobile sales agencies and others. One such company, the Donnelly Corporation, produces the Motor Registration News (MRN). This is published weekly and lists all new car registrations. In addition, a portion of the vehicle identification number (VID) is given. The complete VID contains model year identification information. However, as given in the MRN, the year identification portion for all cars except Fords, Lincolns, and Mercurys is truncated, and is not available.

During the initial phases of the program (late 1974), model year identification was mandatory since both 1974 and 1975 cars were being sold as new cars (registered for the first time). Because of necessity, the 1974-1975 split for the Ford-Lincoln-Mercury group was assumed to be the same as for all other cars. This approach thus gave the 1975 cars registered in Los

Angeles County from the time of their introduction. With a constant automobile population of 3.75 million in Los Angeles County and an estimate of 1975 cars not equipped with the catalytic converter, the percent of cars equipped with the catalytic converter could be estimated. Figure 3 shows a plot of catalyst converter equipped cars (as obtained from cumulative registration information) as a function of time.

In about April 1975, it was learned that the Donnelly Corporation had the complete vehicle identification number (including make and model year information) for all cars in their computer files. It thus became possible to obtain from them the cumulative total of post-1974 vehicle registrations in Los Angeles County as well as the cumulative total of post-1974 vehicles which do not have the catalytic converter. This group includes BMW, Colt, Honda, Mazda, Porsche, and Subaru. Data from this source were first obtained in May of 1975. These data are also plotted in Figure 3, and are identified as "Donnelly Data." The small discontinuity in the plot is caused by the two different methods used. Considering the overall reliability of the method, this discontinuity is trivial.

The data show that as of January 1977, 15.5% of the cars registered in Los Angeles County were equipped with the catalytic converter. The increase averages about 0.6% per month.

A serious flaw has been recognized in this approach since it began to be used. The information obtained is the percentage of cars, which are equipped with the catalytic converter, registered in Los Angeles County and not the percentage of converter equipped cars which pass the LACS site. A TRW report prepared for the California Air Resources Board ("A Mobile Source Emission Inventory System for Light Duty Vehicles in the South Coast Air Basin" - draft copy) contains data which indicate that the newer cars are driven much more than older cars. Therefore, registration information may not be adequate in estimating the number of new cars which are traveling on freeways. In the report, it indicates that for 1975 cars, the miles traveled per vehicle on a normalized basis is 2.04. To obtain this number, the total normalized miles driven by 1975 cars is divided by the total normalized number of 1975 vehicles in the study. For 1974, this normalized value is 1.90, and the value gradually decreases to 0.98 for 1969 model cars and 0.40 for 1964 cars. Because of the greater usage of the newer cars, it is likely that the number of cars equipped with the catalytic converter that travel the freeway (and, therefore, statistically pass the LACS site) is greater than, for example, the January 1977 value of 15.5%. On the basis of this usage, the January 1977 actual percent of converter equipped cars passing the site is more likely between 20 and 30%.

In the beginning of this section, the possibility was discussed of obtaining make and model year identification from the State Department of Motor Vehicles after photographing the license plates of automobiles passing the LACS site. Because of the charge which the state imposes for identifying the vehicle from the license plate number, this approach, if all license plates had to be identified, appeared to be expensive. It has since been found that the State Department of Motor Vehicles has issued license plates serially since the introduction of the "blue background" plates in 1968.

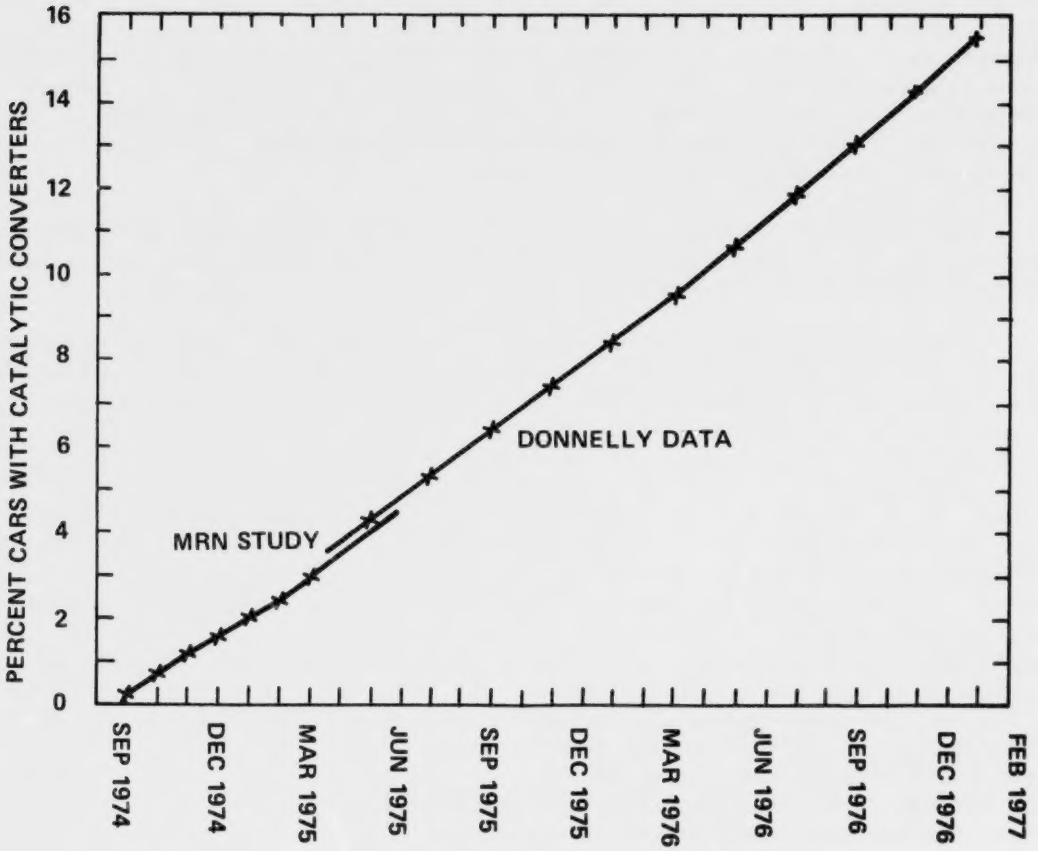

Figure 3. Percent catalytic equipped autos registered in Los Angeles County.

The number of plates, therefore, requiring identification may be significantly decreased making this approach a more viable one.

The "blue background" plates (used in 1968 and later) have three numbers and three letters (e.g. 248 JGN). The DMV has indicated that the letter portion of the plate is serialized and that in September 1974, all license plates sent from the manufacturer to the distributors were marked MXX or with other first letters which follow M in the alphabet. Allowing one letter for the local stock at hand in the DMV offices, it is, therefore, possible to say that all license numbers starting with letter A through K are pre-1975 model, and license plates starting with L to Z may be 1975 or later.

The assignment of L to Z class to post-1974 cars is not definitive, since consideration must be given to the possibility that pre-1975 cars may have been re-registered for some reason (e.g., out of state cars) and, therefore, have a license plate number in the L to Z class. In addition, one must consider the fact that not all post-1974 cars have the catalytic converter.

It appears as if techniques can be used to definitize the number of catalytic equipped cars in the L to Z license plate class, making this an approach which can determine the actual number of cars equipped with the catalytic converter which pass the LACS site. Application of this technique is currently being implemented.

LABORATORY QUALITY CONTROL

George Colovos, Edward P. Parry, and Lloyd S. Shepard

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The internal quality control applied to laboratory analyses of the Los Angeles Catalyst Study manual samples is presented. Included in this discussion are the use of quality control reference samples, quality control on calibration parameters, statistical treatment of the data, establishment of operational quality control limits, development of quality control reports, and establishment of necessary rules for acceptance or rejection of sample data. An early warning system presently in use and future plans for on-line, internal quality control is also presented.

INTRODUCTION

The importance of applying quality assurance control practices to laboratory procedures was recognized very early by chemists; several texts of analytical chemistry devote chapters to this subject. Essentially, the purpose of quality assurance is to answer the question of whether data generated by an analytical procedure can be regarded as typical samples from a single population of data. If such data can be so regarded, statistical control can be assumed. The most commonly used method of determining accurate representation consists of control charts. Control charts are sequential plots of various quality characteristics. For example, qualities shown might be a day-to-day plot of the average content of copper (Cu) in an ore, the normality of a standard solution, the calibration parameters of an instrument, etc. Control charts give a continuous record of the quality characteristic and trends in data. Also, sudden lack of precision can be made evident and causes may be sought by use of the charts. The necessity of comprehensive quality assurance techniques in air quality data generated either in the field or in the laboratory are very well known and have been recognized widely (1). No study can be considered complete without the application of some type of quality assurance procedure. In the case of the Los Angeles Catalyst Study

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(LACS) project, the chemical analysis of integrated samples is vital for the interpretation of air quality data associated with use of catalytic converters on automobiles. For this reason, a comprehensive plan for quality assurance of chemical analysis was conceived and implemented (2).

In this plan, measures for controlling all the possible parameters affecting the quality of data were proposed and implemented. Considered parameters included: chemicals, sample identity, transportation, storage, analytical procedures, personnel, and calibration. In this paper an attempt is made to present the most important features of this program and also to analyze some of the results and discuss some future plans for computerized on-line laboratory quality control.

DISCUSSION

As mentioned previously, the quality assurance plan for chemical analysis of LACS samples included all the parameters associated with the quality of the laboratory results. Although some of the listed parameters are very important for the overall quality of the data, they will not be discussed here because the types of controls recommended for them were more procedural that statistical. Therefore, they could not be used as quality control indicators. Basically, the control limits for these parameters were set forth by establishing procedural protocols which assured the integrity of the samples and/or the application of sound and proven techniques.

The adherence to these protocols were checked by employing quality control of the calibration parameters and by utilizing quality control of the calibration parameters and by utilizing quality control samples. Performance during analyses was checked in the same manner.

The calibration parameters of any analytical procedure can be considered as a measure of accuracy. Therefore, quality control procedures pertinent to each parameter ascertain the degree of uniformity of laboratory data. If the arrived at degree of uniformity is combined with use of primary calibration standards, accuracy obtained for laboratory data can be checked by employing quality control on calibration parameters. Table I lists standards used for calibration of procedures utilized in the analyses of the LACS samples An out-of-control situation of any given batch of analyses can be traced back to these stndards and a determination can be made as to whether the cause of the out-to-control condition was due either to wrong standards or to some other factor. In order to insure complete traceability, all steps involved in the preparation of standards, such as weighings, dilutions, date of preparations, etc, are recorded in a special log book.

The use of quality control samples reveals information about the precision of the analytical procedure. Table II gives the types of control samples employed in analysis of LACS samples along with the frequency of their application. With the exception of the spiked samples, control samples are measures of analytical precision. Control charts made from these data can show trends of precision and out-of-control conditions for any given analysis. The types of control charts utilized in this study are shown in Table III.

TABLE I. STANDARDS FOR ANALYTICAL PROCEDURES

Method	Standard
1. Mass Determination	NBS traceable weights.
2. SO_2 Bubbler	NBS certified SO_2 permeation tube. $Na_2S_2O_5$ reagent grade chemical standardized with iodine-thiosulfate.
3. Sulfate	Standard Na_2SO_4 solution prepared gravimetrically.
4. Nitrate	Standard $NaNO_3$ solution prepared gravimetrically.
5. Ammonium	Standard NH_4Cl solution prepared gravimetrically.
6. Metals (Pb^{++})	Standard metal salt solutions.

TABLE II. INTERNAL QUALITY CONTROL OF THE INTEGRATED SAMPLES OF THE LOS ANGELES CATALYST STUDY

Type of Analysis	Instrumentation	Quality Control Checks
1. Mass Determination	Analytical Balance	Calibration checked daily against a standard weight.
A. Unexposed	Analytical Balance	10% are reweighed
B. Exposed	Analytical Balance	10% are reweighed
2. $SO_4^=$, NO_3^- & NH_4^+	Techicon Auto-Analyzer II	Calibrated daily against standard solutions. Control checks per tray of 40 samples. 1. Extract from previous tray.* 2. Blank extract.** 3. Standard solution. 4. Duplicate exposed strips.
3. Metals (Pb^{++})	Atomic Absorption	Calibration check daily against standard solutions. Control checks per run 1. Two repeat extract. 2. Two blank extracts (one spiked). 3. Two standard solutions. 4. Two duplicate exposed strips.
4. Preparation of SO_2 Bubblers	Repipette	Calibrated daily against a 50.0 ml Type A volumetric flask.
5. Analysis of SO_2 Bubblers	Technicon Auto-Analyzer II	Calibrated daily against standard solutions Control checks per tray of 40 samples. 1. Duplicate solution from previous trays.* 2. Old samples. 3. Standard solution. 4. Another standard solution

*In the first tray, one of the first samples is moved to the end of the tray.

**Once a week one spiked blank.

TABLE III. QUALITY CONTROL GRAPHS

Type of Analysis	Level & Type of Control	Type of Graphs
Mass Determination	10% Reweighed	R-charts for each one.
$SO_4^{=}$, NO_3^{-}, NH_4^{+}, Pb^{++}	Slope, intercept, and error of the calibration curve	R-chart for each parameter.
	Extracts from previous tray	R-charts
	Blanks	R- and S-charts
	Duplicate exposed strips	R-charts
	Spiked samples	% recovery
SO_2	Slope, intercept, and error of the calibration curve	R-charts for each parameter
	Duplicate solutions from previous trays	R-charts
	Old samples	R-charts
	Standard solutions	R-charts
	Spiked samples	% recovery

Most of the charts are range charts (R-charts)(which represent either the difference between two successive values, i.e. repeated analysis of the same extract, duplicate analysis of samples, etc.) or the difference of the experimental value from the expected, (standard) solutions. Figures 1 and 2 show the range charts for the slope of the sulfate standard curve and the duplicate analysis of sulfate in the same extract, respectively. All the chart plotting and the statistical calculations associated with them are done by the PDP-11/35 computer established in the chemistry laboratory greatly facilitating handling of the large number of data generated by internal quality assurance. It should be noted that all the individual data used for the construction of control charts are stored in the computer. Therefore, any other statistical treatment of these data, if necessary, can be done easily.

It is evident that internal quality control through the use of control charts can show if the analytical procedures are under statistical control. However, their use does not completely insure the validity of generated data. Additional information on the validity of data can be obtained by an external quality control system utilizing unknowns and split samples. The external quality control program outlined in Table IV has been implemented for the LACS program and has been discussed in detail by J. Puzak (3) and G. Evans (4). However, the proper use of an internal quality control system can minimize the chances of error and can also reduce the cost of the necessary corrective actions if it is found that the analysis has gotten out-of-control. Establishment of operational control limits which allow the analysis to determine out-control conditions is required in this program; the control limits established from previous data of internal quality control were used as operational control limits. When range charts are utilized for quality control, the lower control limit (LCL) is automatically defined as zero and the upper control limit (UCL) is defined as $3.27\ \bar{R}$, where $\bar{R}$ is the average range in the chart. Operational control limits used in these studies were calculated from the overall range ($\bar{\bar{R}}$) obtained by incorporating all the control data since the initiation of the program and is given by $3.27\bar{\bar{R}}$.

Tables V - X show the operational control limits for various control samples and calibration parameters used in the internal quality control of analytical procedures. In these tables, two values are shown for each control parameter. The two values correspond to two reporting periods (Reports VIII and IX). The first (Report VIII) shows the values which were established at the beginning of the reporting period. The second (Report IX) illustrates the values established by incorporating the data generated in this period with those established in the previous reporting period. Out-of-control conditions during one reporting period were determined by comparing the quality control values against the operation control limits established at the end of the previous reporting period. Usually the reporting period was equivalent to one-quarter of the year. Thus, the operational control limits were revised on a quarterly basis by using all the data gathered from the beginning of the program until the end of the last quarter. The broad base of data used for the estimation of the operational control limits eventually resulted in values which did not fluctuate significantly from quarter-to-quarter, although some of the individual data may vary significantly. The variation indicates that the present operational control limits for all practical purposes should be considered as constants and that no quarterly revision of them is necessary

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                     RANGE CHART OF SO4 REPEATED SAMPLES-- GROUP  2

ORDER    R   DATE    ORDER    R   DATE    ORDER    R   DATE    ORDER    R   DATE    ORDER    R   DATE
  OF  YG/ML            OF  YG/ML            OF  YG/ML            OF  YG/ML            OF  YG/ML
RESULTS SO4          RESULTS SO4          RESULTS SO4          RESULTS SO4          RESULTS SO4
    1   1.5    26       11   0.6    29       21   0.6    35       31   1.7    42       41   0.9    47
    2   0.3    26       12   0.3    29       22   2.1    35       32   2.0    42       42   0.8    47
    3   1.1    26       13   0.5    29       23   1.6    40       33   1.3    42       43   0.3    47
    4   1.1    26       14   1.2    30       24   2.2    40       34   3.5    43       44   0.4    47
    5   0.7    27       15   0.9    30       25   0.2    40       35   0.5    43       45   2.0    47
    6   1.3    27       16   1.2    30       26   2.1    40       36   0.8    43       46   0.9    47
    7   0.9    27       17   0.0    30       27   0.3    40       37   0.9    44       47   0.2    48
    8   2.1    27       18   3.9    35       28   0.0    40       38   1.3    44       48   1.3    48
    9   0.4    27       19   1.7    35       29   0.6    41       39   1.6    44       49   0.8    48
   10   1.2    29       20   4.3    35       30   1.7    41       40   0.2    44       50   0.4    48

                MEAN R = 1.168 YG/ML     UCL = 3.815 YG/ML       STD. DEV. = 0.936
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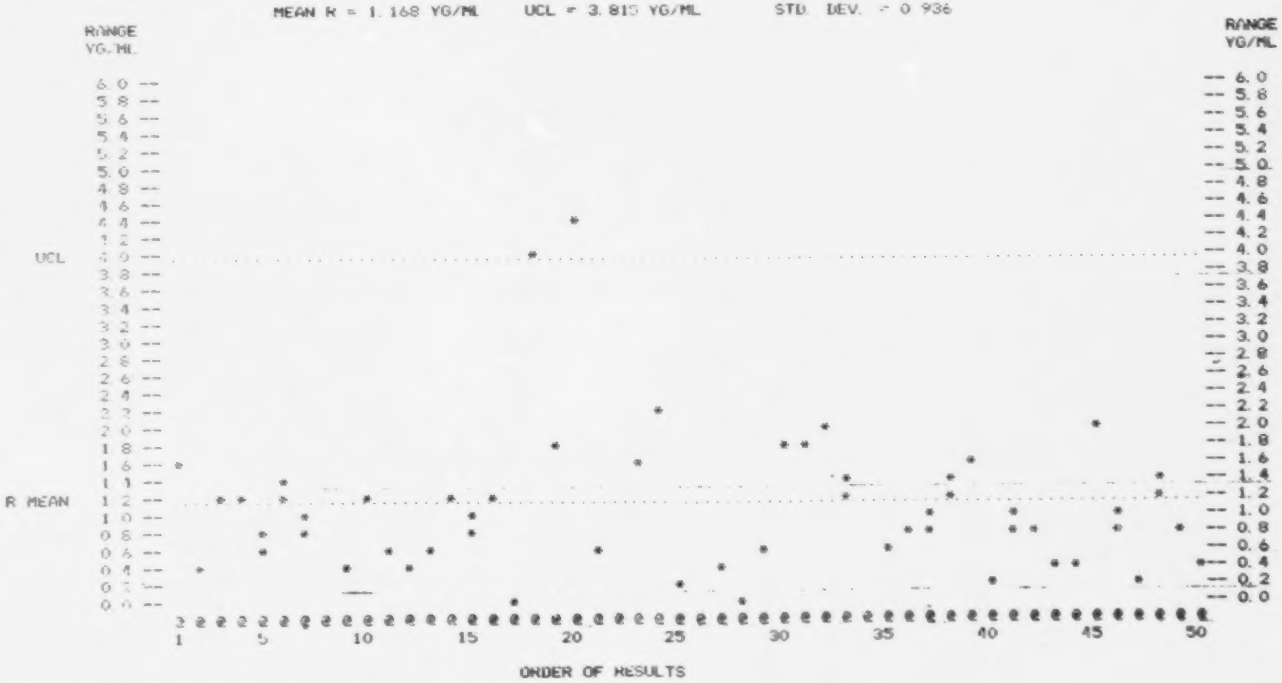

Figure 1. Range chart of the repeated analysis of sulfate in the same extract.

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                       RANGE CHART OF THE SLOPE OF THE S04 STANDARD CURVE--GROUP  2

 ORDER   R    DATE    ORDER   R    DATE    ORDER   R    DATE    ORDER   R    DATE    ORDER   R    DATE
  OF   *100            OF   *100            OF   *100            OF   *100            OF   *100
RESULTS              RESULTS              RESULTS              RESULTS              RESULTS
    1   1.07   26       11   1.19   30       21   1.37   40       31   1.39   42       41   0.45   44
    2   0.61   26       12   0.61   30       22   1.27   40       32   0.07   43       42   1.54   47
    3   0.44   27       13   0.20   30       23   1.42   40       33   0.12   43       43   0.36   47
    4   0.59   27       14   1.86   30       24   1.95   41       34   0.17   43       44   0.61   47
    5   1.30   27       15   0.68   30       25   0.52   41       35   0.57   43       45   0.01   47
    6   1.43   29       16   1.68   35       26   1.22   41       36   1.06   44       46   1.68   48
    7   0.18   29       17   1.86   35       27   0.24   41       37   0.14   44       47   2.11   48
    8   0.49   29       18   0.95   35       28   0.46   42       38   1.11   44       48   0.38   48
    9   0.72   29       19   0.63   35       29   1.46   42       39   1.32   44       49   1.15   48
   10   0.36   29       20   0.26   40       30   1.11   42       40   1.31   44       50   1.42

               MEAN R = 0.908 YG/ML/RE UCL = 2.967 YG/ML/RE    STD. DEV. = 0.566 YG/ML/RE
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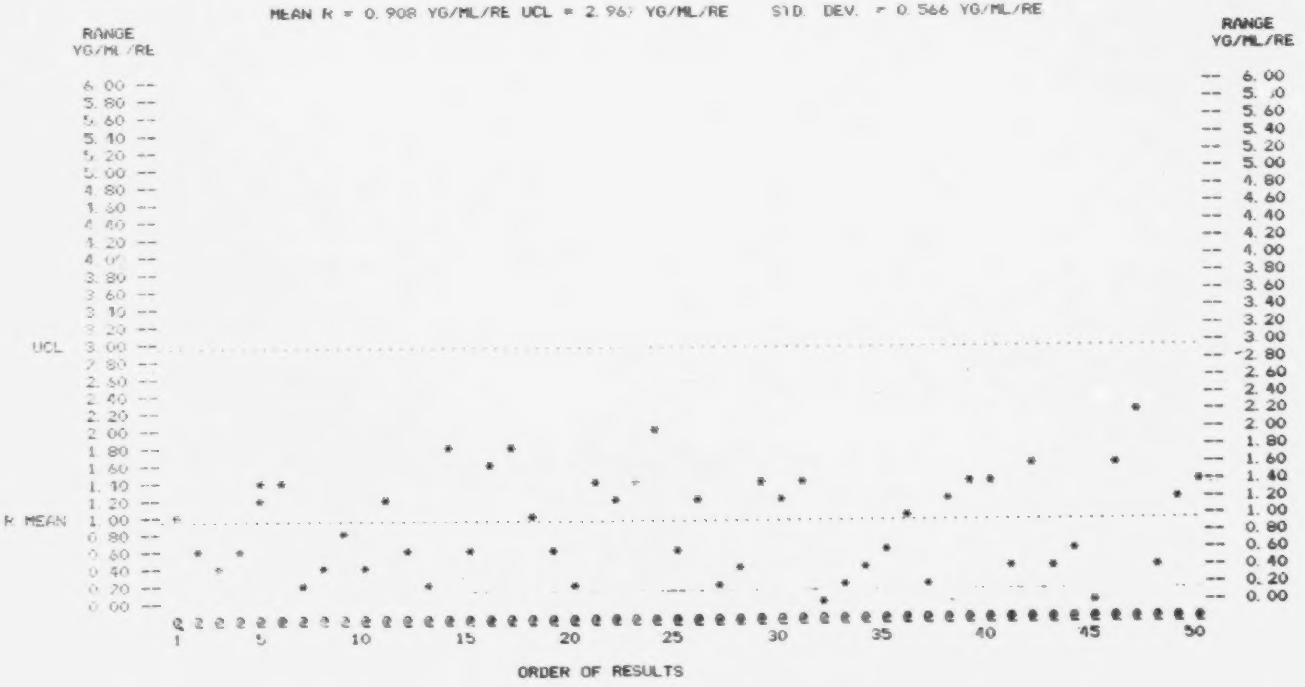

Figure 2. Range chart of the sulfate standard calibration curve.

TABLE IV. EXTERNAL QUALITY CHECKS

Analysis	Exchange Program	
1. Unexposed Filters	Unexposed filters preweighed by the QAB/EMSL of EPA, weighed daily and results reported to EPA on a weekly basis.	2 per day
2. Exposed Filters	8" x 3/4" strips from randomly selected filters corresponding to approximately 5% to the total number of exposed filters sent to EPA for analysis of $SO_4^=$, NO_3^-, NH_4^+ and Pb^{++}. Rockwell reports analytical results simultaneously with the submission of samples.	Once every 3 weeks
	In addition, 10 blind spiked with $SO_4^=$, NO_3^- and NH_4^+ and 7 spiked with Pb^{++} filter strips sent from QAB/EMSL analyzed by Rockwell along with regular samples. Results reported to EPA on a weekly basis. Checks on the mass determination done occasionally by sending exposed filters to EPA.	$\sim$2 per day
3. Bubblers	Blind solutions containing SO_2 sent from QAB/EMSL, analyzed by Rockwell along with regular samples. Results reported to EPA every two weeks.	

TABLE V. CONTROL LIMITS FOR THE
GRAVIMETRIC ANALYSIS OF HI-VOL FILTERS

	$\bar{\bar{R}}$		UCL	
	Unexposed	Exposed	Unexposed	Exposed
Q.C. Report VIII	0.31	0.52	1.01	1.69
Q.C. Report IX	0.31	0.52	1.02	1.70

TABLE VI. CONTROL LIMITS OF THE NO_3^- ANALYSIS

	$\bar{\bar{R}}$		UCL	
	Q.C. Report VII	Q.C. Report IX	Q.C. Report VIII	Q.C. Report IX
Slope	8.24×10^{-3}	7.89×10^{-3}	2.69×10^{-2}	2.58×10^{-2}
Intercept	0.23	0.22	0.75	0.73
Standard Error	8.8×10^{-2}	8.9×10^{-2}	0.29	0.29
Reruns	0.42	0.41	1.39	1.35
Standard Solutions	0.72	0.72	2.36	2.34
Blanks	0.20	0.20	0.66	0.66
Recovery	0.95	0.96	UCL = 1.01 LCL = 0.89	UCL = 1.01 LCL = 0.90
Duplicates	0.40	0.39	1.29	1.26

TABLE VII. CONTROL LIMITS OF THE $SO_4^=$ ANALYSIS

	$\bar{\bar{R}}$		UCL	
	Q.C. Report VIII	Q.C. Report IX	Q.C. Report VIII	Q.C. Report IX
Slope	1.00×10^{-2}	0.99×10^{-2}	3.26×10^{-2}	3.22×10^{-2}
Intercept	0.60	0.59	1.96	1.92
Standard Error	0.20	0.20	0.65	0.64
Reruns	0.92	0.90	3.01	2.93
Standard Solutions	0.86	0.82	2.80	2.69
Blanks	0.80	0.78	2.61	2.55
Recovery	0.96	0.96	UCL = 1.01 LCL = 0.90	1.01 0.91
Duplicates	0.68	0.67	2.22	2.18

TABLE VIII. CONTROL LIMITS OF THE $NH_4^=$ ANALYSIS

	$\bar{\bar{R}}$		UCL	
	Q.C. Report VIII	Q.C. Report IX	Q.C. Report VIII	Q.C. Report IX
Slope	1.49×10^{-3}	1.42×10^{-3}	4.88×10^{-3}	4.65×10^{-3}
Intercept	7.3×10^{-2}	6.9×10^{-2}	0.24	0.22
Standard Error	2.5×10^{-2}	2.4×10^{-2}	8.1×10^{-2}	7.9×10^{-2}
Reruns	0.10	0.10	0.34	0.33
Standard Solutions	0.42	0.37	1.36	1.22
Blanks	9.1×10^{-2}	9.0×10^{-2}	0.30	0.29
Recovery	0.95	0.95	UCL = 1.04 LCL = 0.86	1.03 0.87
Duplicates	0.10	0.10	0.34	0.34

TABLE IX. CONTROL LIMITS OF THE LEAD ANALYSIS

	$\bar{\bar{R}}$		UCL	
	Q.C. Report VIII	Q.C. Report IX	Q.C. Report VIII	Q.C. Report IX
Slope	0.59	0.55	1.92	1.81
Intercept	0.11	0.11	0.37	0.34
Standard Error	$8.6\mathrm{x}10^{-2}$	$8.0\mathrm{x}10^{-2}$	0.28	0.26
Reruns	0.23	0.24	0.76	0.77
Standard Solutions	0.38	0.33	1.22	1.08
Blanks	0.00	0.00	0.00	0.00
Recovery	0.93	0.93	UCL = 0.99 LCL = 0.86	0.99 0.87
Duplicates	0.24	0.21	0.77	0.70

TABLE X. CONTROL LIMITS OF THE ANALYSIS OF SO_2 BUBBLERS

	Q.C. Report VIII	Q.C. Report IX	Q.C. Report VIII	Q.C. Report IX
Slope	$1.78\text{x}10^{-4}$	$1.76\text{x}10^{-4}$	$5.82\text{x}10^{-4}$	$5.77\text{x}10^{-4}$
Intercept	$1.01\text{x}10^{-2}$	$1.01\text{x}10^{-2}$	$3.29\text{x}10^{-2}$	$3.31\text{x}10^{-2}$
Standard Error	$2.66\text{x}10^{-3}$	$2.64\text{x}10^{-3}$	$8.68\text{x}10^{-3}$	$8.62\text{x}10^{-3}$
Reruns	$1.4\ \text{x}10^{-2}$	$1.4\ \text{x}10^{-2}$	4.6×10^{-2}	$4.5\ \text{x}10^{-2}$
Old Samples	$1.8\ \text{x}10^{-2}$	$2.8\ \text{x}10^{-2}$	$9.2\ \text{x}10^{-2}$	$9.0\ \text{x}10^{-2}$
Premeation Tube	$3.3\ \text{x}10^{-2}$	$3.6\ \text{x}10^{-2}$	0.11	0.12
Standard Solutions	$0.9\ \text{x}10^{-2}$	$0.9\ \text{x}10^{-2}$	$3.0\ \text{x}10^{-2}$	$3.0\ \text{x}10^{-2}$

unless the analytical procedures are changed drastically.

Based on the comparison of quality control data obtained during one analytical run with the operational control limits, a determination can be made about the statistical control of generated data. If the calibration parameters were found to be out-of-control, the entire run was considered to be out-of-control and the reason for this was investigated. Essentially, the calibration parameters can get out-of-control either by employing incorrect standards or because of instrument malfunction. In the first case, corrective action consisted of normalizing the results for the difference in the standards. In the second case, the samples were re-analyzed. If calibration parameters were found to be within control but some of the control samples were above the operational control limits, the run was considered to be questionable and the reason for the deviation was investigaged. Again, this problem can be attributed to either the use of an incorrect sample preparation procedure or to an instrument malfunction. In the first case, the run was considered to be within control; no corrective action was taken. In the second case, only the part of the run in which the malfunction occurred (not the entire run) was considered to be out-of-control and requiring re-analyses of the involved samples.

It is evident that any quality assurance procedure, by definition, is an after-the-fact method of evaluating a process. Thus, the corrective actions dictated by the procedure may have serious economic and/or technical impact on the total program. For this reason, quality assurance steps should be taken expeditiously and the corrective actions required applied before irreversible damage, such as invalidation of data, takes place.

In the analysis of LACS samples, a "real-time" internal quality control method was established by which the analyst could evaluate if a particular analysis were in statistical control. The method was accomplished by translating the operational control limits of each control sample or calibration parameter to expected instrument readings which allowed the analyst to evaluate the control data during the performance of the analysis. For example, in the automated analyses, the operational control limits were converted to percent chart reading expected to be obtained for each control sample and, therefore, "real-time"quality control was achieved. The disadvantages of this approach are that the process has to be watched constantly and also that it requires some subjective judgment to be made by the operator. To avoid these limitations a computerized quality control is planned as soon as the analytical instrumentation is interfaced with the laboratory computer. Most of the software for this step has already been developed. The hardware required for the interface has been purchased and installed in the computer. This system will be operational in the very near future. Internal quality control in the chemistry laboratory will therefore, be performed objectively by the computer on real-time.

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EXTERNAL LABORATORY QUALITY ASSURANCE FOR THE LOS ANGELES CATALYST STUDY

John C. Puzak and Thomas A. Clark

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

In order to assess the precision and accuracy of the results reported by the analytical contractor, Rockwell Air Monitoring Center, two separate external quality assurance programs are conducted by the Environmental Monitoring and Support Laboratory. The Quality Assurance Branch supplies the contractor with blind quality control samples, which simulate actual field samples containing sulfate, nitrate, lead, and sulfur dioxide. The Analytical Chemistry Branch of Environmental Monitoring and Support Laboratory performs duplicate [split] sample analyses on approximately 1% of the hi-vol and membrane samples previously analyzed by Rockwell. The blind sample program provides information on the precision and accuracy of the analytical methodology of the contractor. The split sample program provides information on the comparability of the Rockwell laboratory with the Environmental Monitoring and Support Laboratory reference laboratory, Analytical Chemistry Branch.

INTRODUCTION

Before awarding the contract for the Los Angeles Catalyst Study (LACS), the Environmental Monitoring and Support Laboratory (EMSL) of the Environmental Protection Agency (EPA), was concerned about the quality of the data that would be produced during the study. In order to verify and document the quality of the data, two forms of quality assurance were contained in the original contract. An internal quality assurance program was to be conducted by the contractor and an external quality assurance program would be conducted by EMSL. The external quality assurance for the analytical laboratory was to consist of two parts, split sample analysis and blind audits.

A split sample analysis quality assurance program was initiated in July of 1974 when collection of air samples began in LACS. Aliquots of the air samples are analyzed by the contractor, Rockwell Air Monitoring Center (RAMC), and the Analytical Chemistry Branch (ACB), EMSL. The split sample program was begun to determine the comparability between analyses performed by RAMC and EMSL and to determine analytical variability on real air samples.

In November of 1974 a blind audit quality assurance program was initiated for RAMC by the Quality Assurance Branch (QAB), EMSL. The blind Audit program

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was initiated to investigate and document the precision and accuracy achieved by RAMC during the analysis of ambient air samples collected in LACS.

Both the blind audit and split sample program have changed since their beginnings in 1974 to accommodate fluctuations in the number of samples collected in LACS, variability of the analytical results, and EMSL's growing experience in conducting external audit programs. Table I gives the pollutants, types of audit sample and frequencies of both the blind audit and split sample programs used in the last quarter of 1976 and the first quarter 1977 for RAMC analyses.

Sulfate and nitrate are spiked on the same filter for the blind audit samples: lead (Pb) is spiked on a separate filter. RAMC must then extract and analyze these samples as they would an ambient air high volume (Hi-Vol) sample. Sulfur dioxide (SO_2) blind samples are special freeze-dried tetrachlormercurate-sulfite solutions. RAMC must thoroughly rinse the audit sample from a sealed vial with absorbing reagent before analyzing as a normal 50 ml bubbler sample.

The samples used for blind audits have all been developed by QAB as part of its program for assisting analytical laboratories to improve their in-house analysis capabilities. Each lot of samples is analyzed by QAB and a corroborative laboratory before it is accepted for use in the blind audit program. The QAB analysis, the corroborative analysis, and the attempted spike must agree to within 5% and the relative standard deviation, for a spike level must be less than 2.5% or the samples are rejected.

The split samples consist of duplicate 3/4" x 8" filter strips cut from exposed Hi-Vol filters, collected at the LACS stations. These filters are sent to ACB and RAMC for analysis. Sulfur dioxide air samples are not split because collected samples decompose with time.

PURPOSE OF SPLIT AND BLIND AUDIT PROCEDURES

The main use of the blind audit results is to document chronologically the precision and accuracy achieved by RAMC. EMSL has decided that a meaningful way to display the chronological precision and accuracy is through mean and range control charts. The control chart format conveniently displays precision and accuracy versus time and also provides criteria to judge whether the analytical methods used by RAMC exhibits acceptable variability or are subject to greater than normal fluctuations. The common usage of control charts to detect and immediately correct any analytical irregularities cannot be applied because of the one to two week delays involved in transmitting the results to EMSL. Corrective action on analytical problems is based on RAMC's internal quality control data.

A second major use of the blind audit data is to determine if any portions of the analytical methods employed by RAMC need improvement. This use will be illustrated in the Results section which discusses low-level sulfate variability and the corrective measures that were needed.

The third use of the blind audit results is to point out a large bias or

TABLE I. BLIND AUDIT AND SPLIT SAMPLE FREQUENCIES

Pollutant	*Sample Type*	*Audit Frequency* *Blind Audit*	*Split Sample*
Sulfate	*Hi-Vol Filter*	*10/week*	*6/month*
Nitrate	*Hi-Vol Filter*	*10/week*	*6/month*
Lead	*Hi-Vol Filter*	*7/week*	*6/month*
Sulfur Dioxide	*Bubbler*	*10/bi-weekly*	*None*

variability that might occur across all levels for a pollutant during an analytical period. If this situation occurs, both the EPA project officer and RAMC are immediately notified. This situation has never occurred during the blind audit program.

Since the blind audit samples are not real air samples, but synthetic samples, the split sample program serves to show variabilities encountered on analysis of real samples. Secondly the split sample results serve as a measure of the reproducibility on real samples between two laboratories which are using the same analytical methods. Initially the split sample program was conducted at a much higher analysis rate than is shown in Table I, but the larger time delay between analyses, the information obtained in the blind audit results, and the continuing comparability between ACB and RAMC, allowed EMSL to cut back to the current split sample rate.

Summary reports for both blind and split sample analysis are periodically made to the EPA project officer and to RAMC. Split sample results are reported at the end of each quarter, while blind audit results are reported at twenty-five week intervals.

SPLIT AND BLIND AUDIT PROCEDURES

SPLIT SAMPLE PROGRAM

Samples to be used for split analysis are randomly selected by RAMC from the Hi-Vol samples collected in LACS. Extra 3/4" x 8" strips are cut from the Hi-Vol filters and sent to ACB where they are analyzed once per quarter. Results from both analyses are compared by the EPA project officer. Limits of ±10% or 1 $\mu g/m^3$, whichever is larger, are the acceptable limits for the differences between the two laboratories for all pollutants. If differences are outside these limits, further action such as reanalysis by one or both laboratories, is usually taken. If significant differences do occur in the split sample program the blind audit results for the same period are also evaluated and corrective action is based on a combination of the results from both audit programs.

BLIND AUDIT PROGRAM

Periodically (see Table I for frequency) a set of samples for sulfate/nitrate, Pb, and SO_2 are sent to RAMC for blind audit purposes. Table II shows the quantity per level for each blind audit set. RAMC distributes the audit samples as evenly as possible among the analysis days during the audit period and intersperses the audit samples throughout their normal analysis of LACS air samples.

On the last day of the audit period the results for all audit samples analyzed are reported to QAB. When the results are received by QAB the mean and range are determined for each pollutant level and plotted on their respective control charts. The means and ranges reported for all sulfate, nitrate, Pb, and SO_2 blind audits conducted during a twenty-five week period are used to determine a grand mean ($\bar{\bar{x}}$) and a mean range ($\bar{R}$) for each pollutant spike level. Outliers and out of control results are not included in the

TABLE II. DISTRIBUTION OF BLIND AUDIT SAMPLES ACROSS ANALYTICAL RANGE

	SO_2, SO_4 and NO_3 Number of Samples/Set	P_B Number of Samples/Set
High Level	3	2
Mid Level	3	2
Low Level	3	2
Blanks	1	1
Total:	10	7

calculation of $\bar{\bar{x}}$ and $\bar{R}$. The grand mean and mean range can then be used to calculate control chart limits which will be used for the next twenty-five weeks of blind audits. Thus, the control limits are revised if necessary, every twenty-five weeks.

The construction of control limits will be illustrated using sulfate blind audit results. The control chart limits can be determined from the equations given in Table III; $\bar{\bar{x}}$ values for the control charts are the spike value times the average recovery shown in the previous twenty-five weeks of analysis. $\bar{R}$ is taken from a plot of mean range versus mean results for each spike level for a particular pollutant. Figure 1 gives a plot of mean range versus grand mean for RAMC blind audit sulfate results in the last twenty-five weeks of 1976. The $\bar{R}$ to be used for control limit calculations are read from the curve at the x-axis value corresponding to the spike levels to be used in the next series of blind audits. Figure 2 gives an example of a sulfate mean and range control chart for a sample corresponding to about 20 $\mu g\ SO_4/m^3$. A similar pair of control charts would be made up for each different sulfa spike level.

Besides the control chart display the blind audit reports determine the average recovery for each analytical method audited. The average recovery for a method is defined to be the slope of the least squares linear regression of the mean of the reported values versus the spike value.

Since there is so much data collected over a twenty-five week audit period, plots of reported analysis versus spike value will be used to summarize the blind audit results in the remainder of this paper.

RESULTS OF BLIND AND SPLIT SAMPLE AUDITS

SULFATE

A plot of RAMC mean sulfate analysis versus spike value for audits conducted during the last twenty-five weeks of 1976 is shown in Figure 3. Each triangle represents the mean of 15 to 18 RAMC analyses. The slope (0.974) and small scatter about the regression line indicate very good average recovery for the sulfate analytical method over its entire range. The numbers in parentheses on the y-axis indicate the coefficient of variation for RAMC analyses at the indicated sulfate level. These values, below 6% over the entire range, show good precision for the RAMC sulfate analyses. The values in parentheses on the x-axis are the ambient air concentrations in $\mu g\ SO_4/m^3$ which correspond to the μg of sulfate found on a 3/4" x 8" strip from a twenty-four hour Hi-Vol sample.

The agreement of results below 500 μg (10μg/ml of filter extract) was achieved only by reanalyzing the extracts by a sulfate procedure that is 10 times more sensitive than the routine sulfate procedure used by RAMC to analyze LACS air samples. Table IV compares the analytical results for blind audit samples containing less than 500μg of sulfate/strip obtained by both the routine and sensitive procedures. A marked improvement in both precision and accuracy is achieved by using the sensitive procedure to analyze these sulfate samples. Because of these findings RAMC now reanalyzes all filter

TABLE III. CONTROL LIMITS FOR BLIND AUDIT MEAN AND RANGE CONTROL CHARTS

Range Control Charts

Upper Control Limit (UCL) = $D_4 \bar{R}$

Lower Control Limit (LCL) = $D_3 \bar{R}$

Mean Control Charts

$UCL = \bar{\bar{X}} + A_2 \bar{R}$

$LCL = \bar{\bar{X}} - A_2 \bar{R}$

$\bar{R}$ = Mean of Weekly Ranges

$\bar{\bar{X}}$ = Mean of Weekly Means

D_3, D_4, and A_2 are control chart factors from Duncan, Acheson J. *Quality Control and Industrial Statistics*, 968-969, Fourth Edition (1974), Richard D. Irwin, Inc.

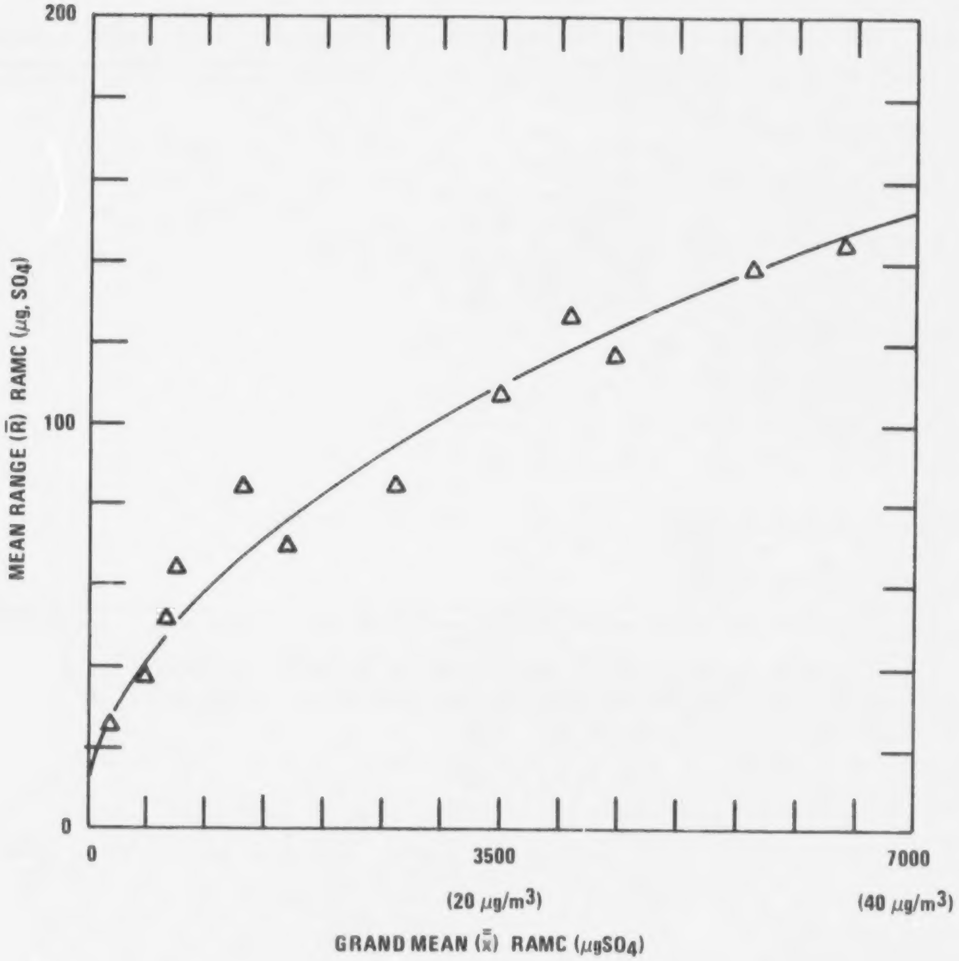


Figure 1. Range versus mean for RAMC blind sulfate analysis (1976).

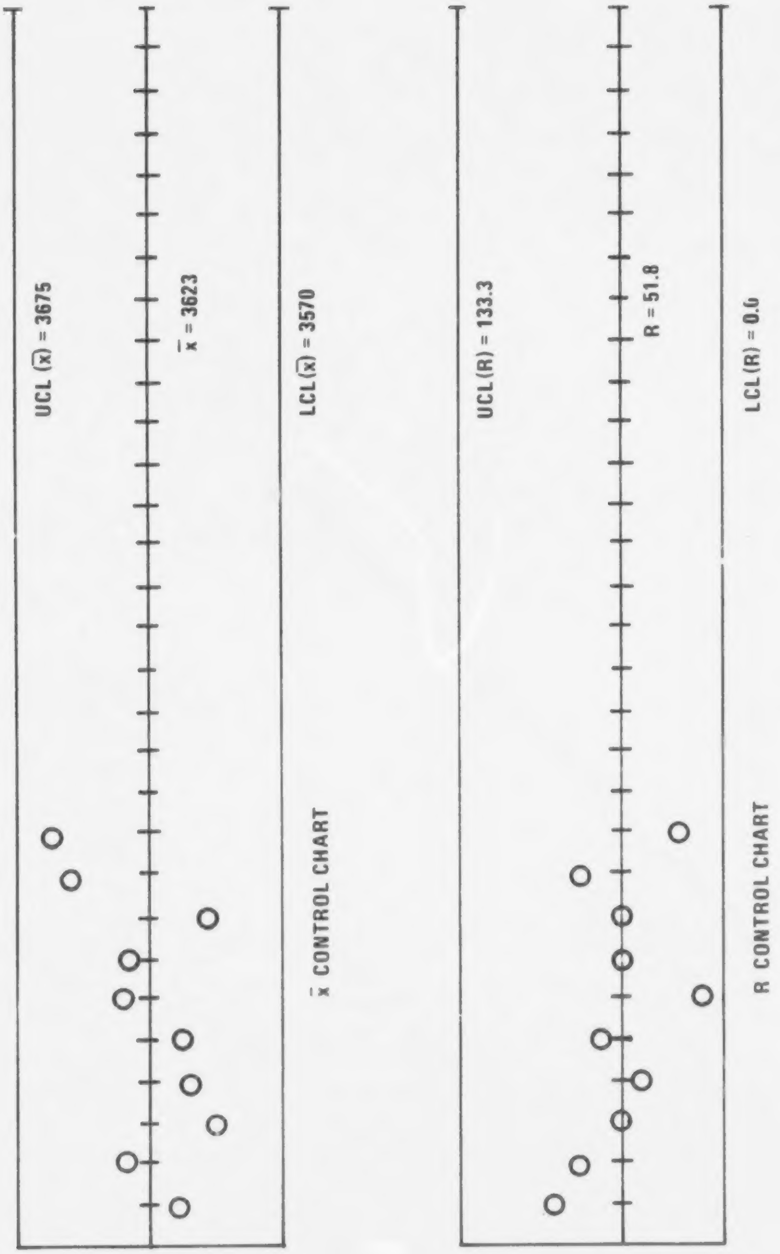


Figure 2. Sulfate Control Charts.

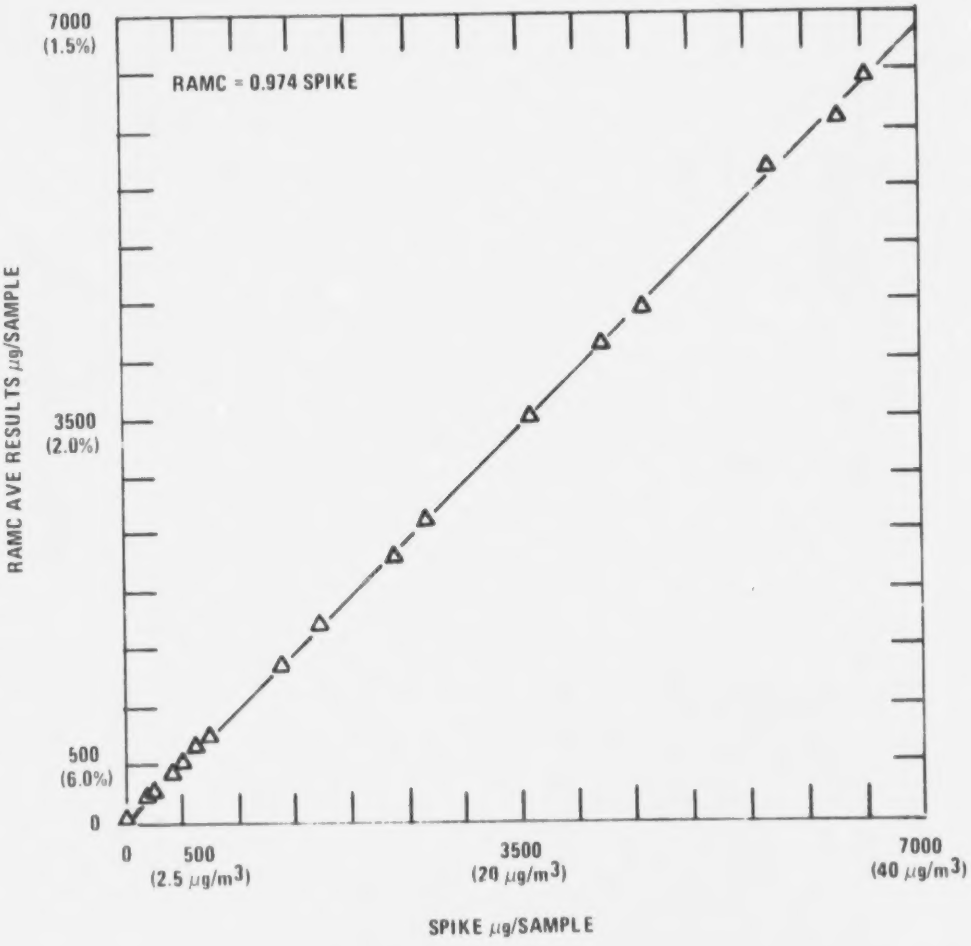


Figure 3. Comparison of RAMC blind sulfate results with spike values.

TABLE IV. COMPARISON OF RAMC ANALYSES OF LOW LEVEL SULFATE BLIND AUDIT SAMPLES BY SENSITIVE AND ROUTINE SULFATE METHODS

Spike Total μg	ROUTINE METHOD Mean Total μg	ROUTINE METHOD Std. Deviation	SENSITIVE METHOD Mean Total μg	SENSITIVE METHOD Std. Deviation
0 (Blank)	164	33	20	18
200 (1.0 $\mu g/m^3$)	317	33	200	12
250	319	40	261	16
405	464	38	408	18
498 (2.5 $\mu g/m^3$)	512	25	484	24

extracts which fall below 10 μg SO_4/ml by their sensitive sulfate procedure.

The split sample results from the first quarter of 1977 show agreement between RAMC and ACB to within 5%.

NITRATE

A plot of the RAMC blind nitrate results versus the spike value for the last twenty-five weeks of 1976 is shown in Figure 4. Again, each triangle represents the mean of 15 to 18 RAMC analyses; the coefficient of variation of the RAMC analysis is indicated in parentheses on the y-axis; and the ambient air concentration corresponding to a twenty-four hour Hi-Vol sample is in parentheses on the x-axis. The slope (0.972) and scatter about the regression line indicate good recovery down to about 300 μg NO_3 per sample (6 μg NO_3^- /ml of filter extract). Results below 300 μg NO_3^- are more variable and are less accurate. A coefficient of variation of less than 4% over the analytical range indicates that precision for nitrate analyses is excellent.

Since the actual nitrate levels found in the LACS air samples are usually greater than 5 μg/m^3 or 1000 μg/strip, no great effort has been made to improve the method at low nitrate levels. Audit results for nitrate have been similar to these since the blind audits began in November 1974.

The split sample results for samples collected in July and August 1974, however, showed a difference between RAMC and ACB that was greater than the acceptable limits. Table V gives examples of the split sample differences that occurred in 1974. Investigation found that RAMC nitrate standard solutions used in July and August had been improperly prepared. RAMC records were complete enough so that recalculating the results was the only corrective action that was necessary.

First quarter 1977 split sample results for nitrate indicate agreement between RAMC and ACB to within 5%.

LEAD

Figure 5 gives two plots for RAMC blind Pb results versus the spike values. The triangles represent audit data from 1976 and the squares represent audit data from 1975. Each triangle is the mean of 10 RAMC analyses and each square is the mean of 18 to 30 RAMC analyses. The coefficient of variation of RAMC analyses is shown in parentheses on the y-axis and the ambient air concentration for a twenty-four hour Hi-Vol sample is shown in parentheses on the x-axis. The slope for the 1976 results is 0.871 and the slope for the 1975 results is 0.900. The RAMC blind Pb results have consistently been 10% to 12% low since audits were started in 1975. RAMC is investigating their Pb extraction and analysis procedure during the first quarter of 1977 to see if recoveries can be improved. The coefficient of variation is less than 3%, which indicates that precision of blind Pb analyses is excellent.

The Pb split sample analyses performed in late 1974 and early 1975 showed the variable percent differences given in Table VI. A detailed

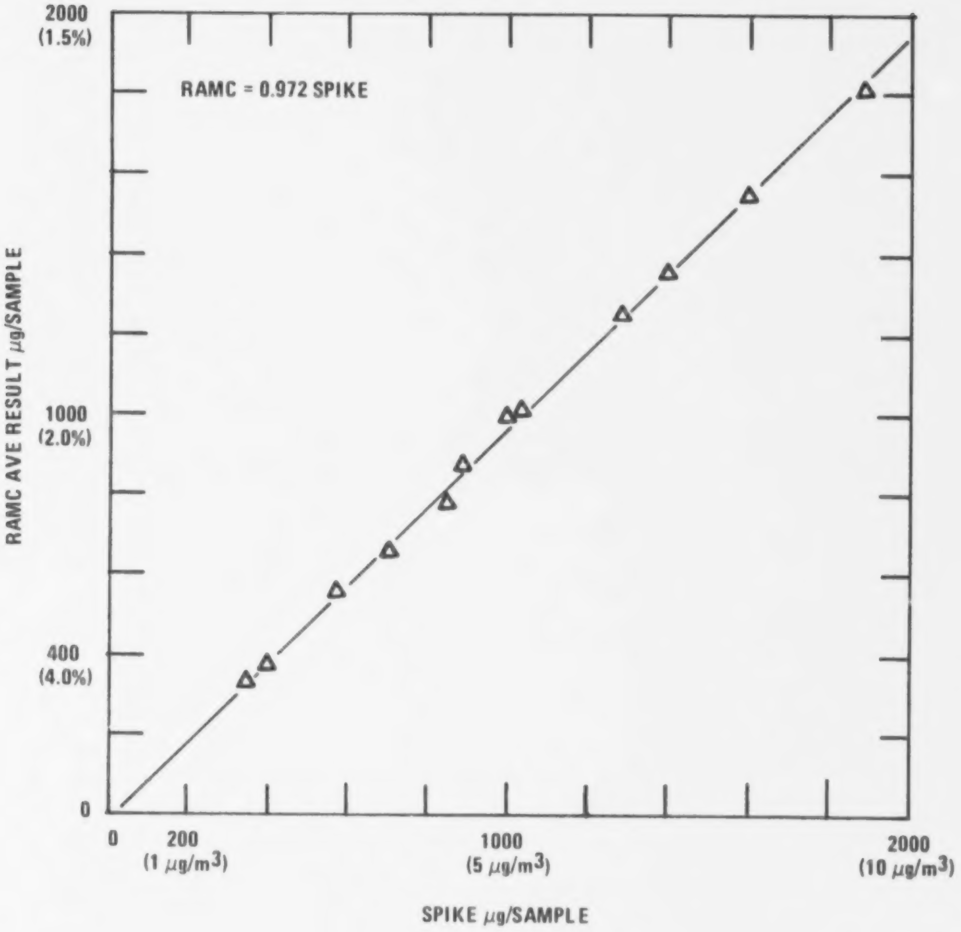


Figure 4. Comparison of RAMC blind nitrate results with spike values.

TABLE V. NITRATE SPLIT SAMPLE DIFFERENCES - AUGUST 1974

RAMC ($\mu g/m^3$)	EMSL ($\mu g/m^3$)	% Difference
10.97	9.90	+ 10.3
8.74	7.20	+ 19.3
21.72	18.30	+ 17.1
19.45	17.50	+ 10.6
7.03	5.90	+ 17.5
15.40	13.10	+ 16.1
11.29	8.80	+ 24.8

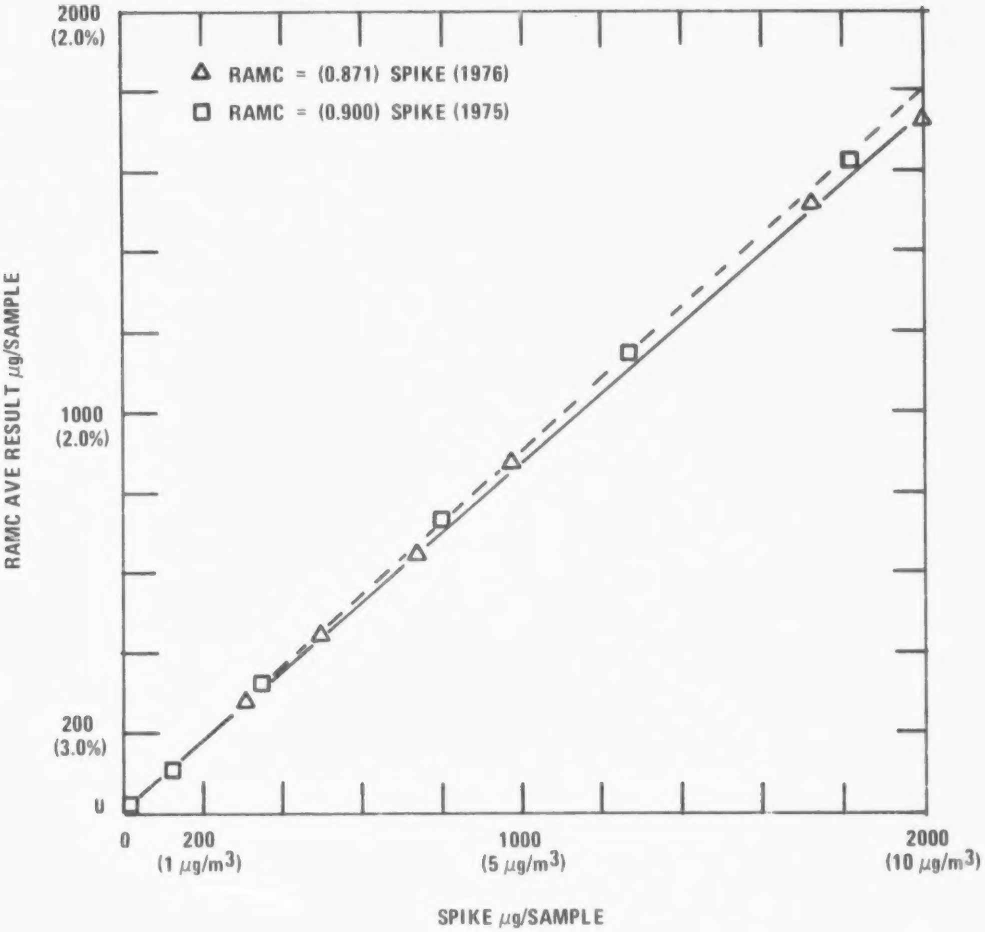


Figure 5. Comparison of RAMC blind lead results with spike values.

TABLE VI. LEAD SPLIT SAMPLE DIFFERENCES (AUGUST - DECEMBER 1974)

RAMC	EMSL	% Difference
4.60	4.65	-1.1
4.30	13.55	-103.6
4.30	7.83	-50.2
9.50	12.40	-26.5
1.70	2.93	-53.1
2.70	2.88	-6.5
10.50	12.63	-18.4
7.00	6.89	+1.6
3.70	6.34	-52.6

investigation of both ACB and RAMC Pb analytical procedures using real and synthetic Hi-Vol samples showed an equipment malfunction and contamination in the ACB extraction procedure. The RAMC results for LACS analyses were accepted and the ACB extraction apparatus was modified and moved to improved facilities.

First quarter 1977 Pb split analysis shows agreement between RAMC and ACB to within 10%.

SULFUR DIOXIDE

Figure 6 gives a plot of RAMC SO_2 *blind audit results versus the spike value. Each triangle represents the mean of 15 to 30 RAMC* SO_2 *analyses. The coefficient of variation of the RAMC analyses is given in parentheses along the y-axis and the corresponding ambient air concentration is given in parentheses on the x-axis. The slope of the line (1.043) indicates good agreement with the spike value. Results similar to these have been obtained since the beginning of the blind audit program.*

Because of the temperature instability of the SO_2 *bubbler samples, no split sample analyses have been attempted.*

CONCLUSIONS

The external quality assurance program consisting of split and blind sample analyses has been quite useful in improving, verifying and quantifying the quality of data obtained in LACS. Both the Pb and sulfate analytical procedures have been improved because of the results obtained in the external audit program. Detection and correction of analytical problems has been timely enough to avoid invalidating large blocks of analytical data. Besides upgrading analytical methods, a chronological history of accuracy and precision is available from the start of this project. The results show that an external quality assurance program can be a valuable part of an air monitoring project.

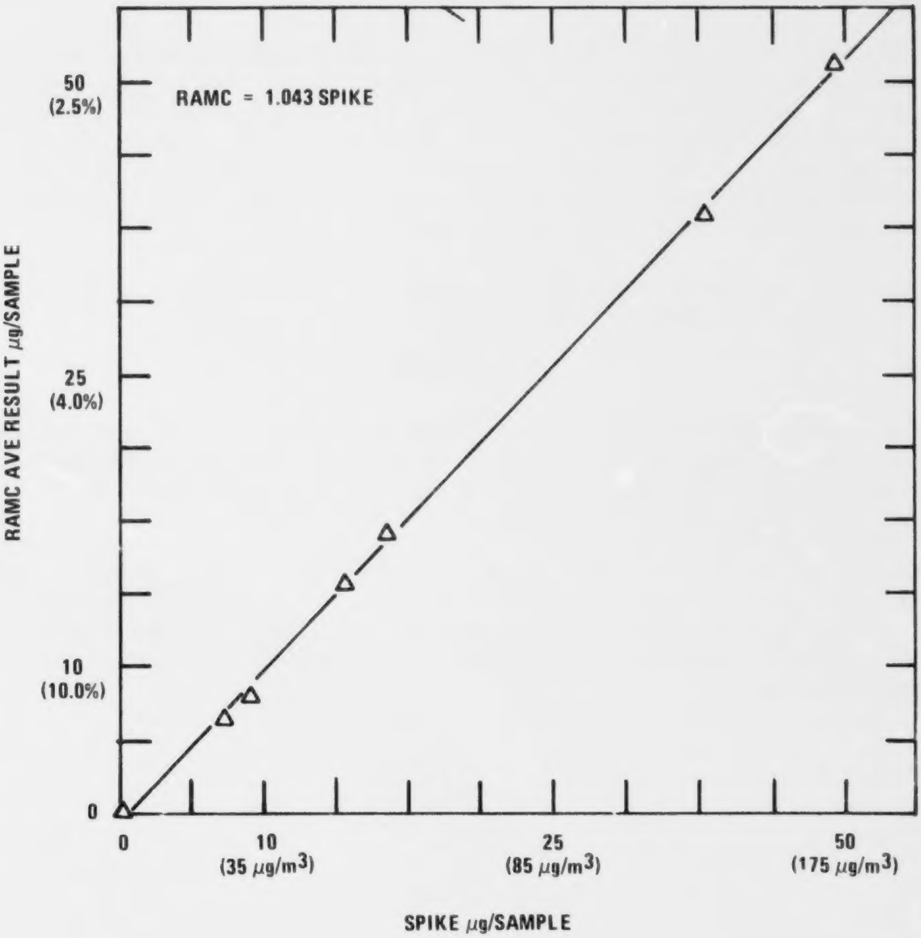


Figure 6. Comparison of RAMC blind sulfur dioxide result with spike values.

THE QUALITY ASSURANCE PROGRAM EMPLOYED DURING SAMPLING

Charles E. Rodes, Bobby E. Edmonds, and Malcolm C. Wilkins

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

This paper describes an extensive quality assurance program involving sampling equipment used in the Los Angeles Catalyst Study. This quality assurance activity is completely separate from quality assurance measures taken during analysis of integrated samples. The program generally consists of dynamic pollutant level checks of the continuous instruments and flow calibration checks of the integrating samplers. The discussion covers the types of internal and external checks used and typical data from various categories of samplers. It also presents results from an external test of field equipment performed by a person not involved in the field program. External audits generate audit information on the accuracy of the sampling equipment. These audits also provide comparability between routine on-site checks and reference materials kept at the Environmental Protection Agency, Research Triangle Park, North Carolina.

INTRODUCTION

The Environmental Monitoring and Support Laboratory (EMSL) has conducted an extensive Quality Assurance (QA) program on all monitoring activities of the Los Angeles Catalyst Study (LACS). The purposes of the QA programs utilized during LACS ambient air monitoring operations are to: (1) provide the precision required using a given method; and (2) provide comparability information to relate, through primary and secondary standards, the data collected by contractor and Environmental Protection Agency (EPA) laboratories. This study is comprised of essentially two separate operations — one carried out on-site, using continuous and integrated sampling in the field, and one which carries out analysis of integrated samples in the laboratory. Separate QA programs are therefore followed.

The sampling methodologies can be divided into two categories: (1) those that monitor continuously and produce in situ hourly averages, and (2) those that collect samples integrated over a selected time interval. The continuous samplers are calibrated by introducing known quantities of the pollutant of interest or comparing their performance with reference samplers. The flow rates of integrated samplers are calibrated against reference flow devices. Additional Quality Assurance measures in support of the monitoring effort include:

- *keeping daily record logs of maintenance and subsystem sampler performance,*
- *providing written operation and calibration procedures for all equipment,*
- *conducting unscheduled performance tests on instrument operations by an individual other than the site operator, and*
- *data validation.*

CONCLUSIONS

The quality of data being generated by the Los Angeles Catalyst Study (LACS) is monitored very closely. The quality assurance elements employed in the LACS sampling operations are the same as those employed in all other Environmental Monitoring Branch (EMB) studies.

As demonstrated by examination of the routinely collected internal audit and calibration information and the results of external audits, the data quality of all measurements at the LACS is very good compared to most field studies. In any large study such as LACS where there are multiple operators, sites, and samplers, some problems usually occur. The quality assurance programs serve the function of not only minimizing errors and quantifying precision, but also pointing out problem areas for subsequent correction. Without a quality assurance program, the data collected are virtually indefensible — for nearly any purpose. The QA information is indispensible in that it defines specifically which data sets are within study tolerance limits for validation purposes, and provides a means in some cases of correcting invalid data.

The only element remaining to be formulated in the LACS sampling QA program is a procedure to compile the collected check and calibration data to provide readily available summary QA statistics along side the data summaries being presented.

DEFINITIONS

For the purposes of this study, the following nomenclature for several types of calibration materials and audits which are referred to in this paper was established.

External audit: An independent calibration test performed by an individual other than the routine site operator(s). This test is typically performed with separate working standards and calibration apparatus supplied by the individual performing the audit.

Internal audit: A calibration test performed by the site operator on the sampling equipment other than a scheduled multi-point calibration. Routine zero and span checks on continuous samplers and periodic one or two point flow checks are internal audit procedures.

Transfer standard: Any standard which is calibrated against primary standard materials. This includes the National Bureau of Standards (NBS) traceable volumetric flowmeter in the laboratory, the gravimetrically calibrated sulfur dioxide (SO_2) permeation tubes, and the cylinders of compressed gas calibrated in the laboratory against NBS traceable materials.

Working standards: A standard used routinely and often prepared in quantity, which is calibrated against the "transfer standard." This includes the routine span cylinders used to check and calibrate the continuous instruments, and the flow orifices used to calibrate the integrating samplers.

INTERNAL SAMPLING QUALITY ASSURANCE PROGRAM

For the LACS program, all quality control measures that do not fall under the definition of "external audit" are considered "internal." These "internal" audits will be discussed for continuous and integrating sampler methodologies.

CONTINUOUS POLLUTANT SAMPLERS

The carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO_2) and ozone (O_3) analyzers are calibrated against compressed gas working standards. The CO instruments which operate at 0-50 ppm full scale are calibrated using cylinders of 40 ppm CO in air, which are certified against a "transfer standard" cylinder. The NO channel (0-1.0 ppm full scale) of the NO/NO_2 instrument is calibrated by diluting a "working standard" mixture of 100 ppm NO in nitrogen. The NO_2 channel (0-0.5 ppm full scale) is calibrated by gas phase titration (GPT) of the "working standard" NO mixture with O_3 to produce specific concentrations of NO_2. The O_3 samplers are also calibrated using the NO "working standard," but utilizing reverse GPT between the NO mixture and a generated source of O_3. Since there is one "working standard" cylinder of each type gas (CO and NO) at each instrumented site, a "transfer standard" cylinder of each type is used to provide a common reference between sites.

The Total Sulfur (S) analyzers (0-0.10 ppm full scale) are calibrated using SO_2 permeation tubes, which qualify as both "transfer standards" and as "working standards." These tubes are calibrated in the laboratory gravimetrically on a recording microbalance and sent to the field as needed. They typically have an SO_2 output of 0.2 μl/min to provide calibration points in the 0-0.10 ppm range.

All continuous pollutant instruments are calibrated with a "zero" and four upscale points. These calibrations are performed monthly with checks of the "zero" and a single 80% span (upscale) point made on a more frequent basis. Table I lists the continuous instruments and the frequency of these checks.

The frequency of 1-point spans is determined from past history of the type of instrument being used, balanced against the total time required to perform the check. The latter item not only requires manpower, but also results in data lost during the span operation. The Total Sulfur analyzers at LACS require over 1 hour for a zero and single point span operation.

TABLE I. FREQUENCY OF CONTINUOUS SAMPLER CHECKS

POLLUTANT	PRINCIPLE	5-POINT CALIBRATION	"ZERO"	1-POINT SPAN
CO	NDIR*	MONTHLY	DAILY	DAILY
NO	CHEMILUMINESCENCE	MONTHLY	DAILY	WEEKLY
NO_2	CHEMILUMINESCENCE	MONTHLY	DAILY	WEEKLY
O_3	CHEMILUMINESCENCE	MONTHLY	DAILY	WEEKLY
TOTAL S	FPD**	MONTHLY	DAILY	WEEKLY

* NON-DISPERSIVE INFRARED

** FLAME PHOTOMETRIC DETECTION

Especially for the CO analyzers the monthly calibration becomes little more than a linearity check, since the span adjustments are reset as needed. These tolerances were established subjectively based on study requirements and past performances of the same types of analyzers.

The % chart values in Table II indicate for the operators how precise the unadjusted readings of a "zero" or upscale point should be before corrective action is taken. Again these limits are based on past records and cost-effectiveness. If a zero or span gas input is made and the sampler response falls within the respective "Tolerance" listed, no adjustments are made. If the response falls outside the tolerance band, but within the "Recalibration Limit," the sampler "zero" or "span" is readjusted. If the response falls outside the "Recalibration Limit," the sampler is considered as working improperly, and a service check performed, followed by a complete recalibration.

The plot in Figure 1 of the CO "zero" drift data for a typical month illustrates the type of information available from daily checks. Note that only 2 unadjusted "zero" checks (5th and 6th) were outside the acceptable ±1.0% band. Apparently on the 5th day an improper "zero" calibration was performed which provided an erroneously high reading. Readjustment by the operator followed by a correct "zero" on the 6th resulted in a negative "zero" that was outside the readjustment band. The problem did not recur during the rest of the month.

A procedure for adjustment of data possibly affected by out-of-tolerance response is also delineated. If the instrument "zero" and "span" are within the "Recalibration Limit," the data collected are adjusted for monotonic zero change only, back to the previous acceptable "zero" check. No attempt is made to correct for span errors, since the instruments have linear response characteristics. If the instrument checks are outside the "Recalibration Limit" all data is voided back to the last acceptable "zero" and "span."

As a check on span gas stability and to provide comparability between "working standard" gas cylinders, "transfer standard" cylinders are calibrated periodically in the laboratory and sent to the field site. These "transfer" cylinders are then used to check the calibration of the "working standards" and calibrate new ones as old ones become exhausted. The "working standard" calibrations are also checked just before being depleted against the transfer standard to verify stability.

The flowmeters on the continuous samplers are not calibrated individually (except in special cases), as their calibration is inherent in the dynamic sampler calibration. The mass flowmeters built into the calibration systems are calibrated on a quarterly basis.

INTEGRATING POLLUTANT SAMPLERS

The high-volume samplers (hi-vols), 102 mm membrane samplers, and dichotomous samplers are calibrated for flowrate measurement. In all cases the "transfer standards" for flow measurement are calibrated against NBS traceable

TABLE II. LACS INSTRUMENT ADJUSTMENT TOLERANCES

POLLUTANT	ZERO TOLERANCE* % CHART	SPAN TOLERANCE* % CHART	RECALIBRATION LIMIT** % CHART
CO	± 1.0	± 3.0	± 5.0
NO	± 1.0	± 3.0	± 5.0
NO_2	± 1.0	± 3.0	± 5.0
O_3	± 1.0	± 3.0	± 5.0
TOTAL S	± 2.0	± 5.0	± 5.0

* BEFORE ADJUSTMENT IS REQUIRED.

** SAMPLER MUST BE RECALIBRATED IF UNADJUSTED SPAN OUTSIDE THIS LIMIT.

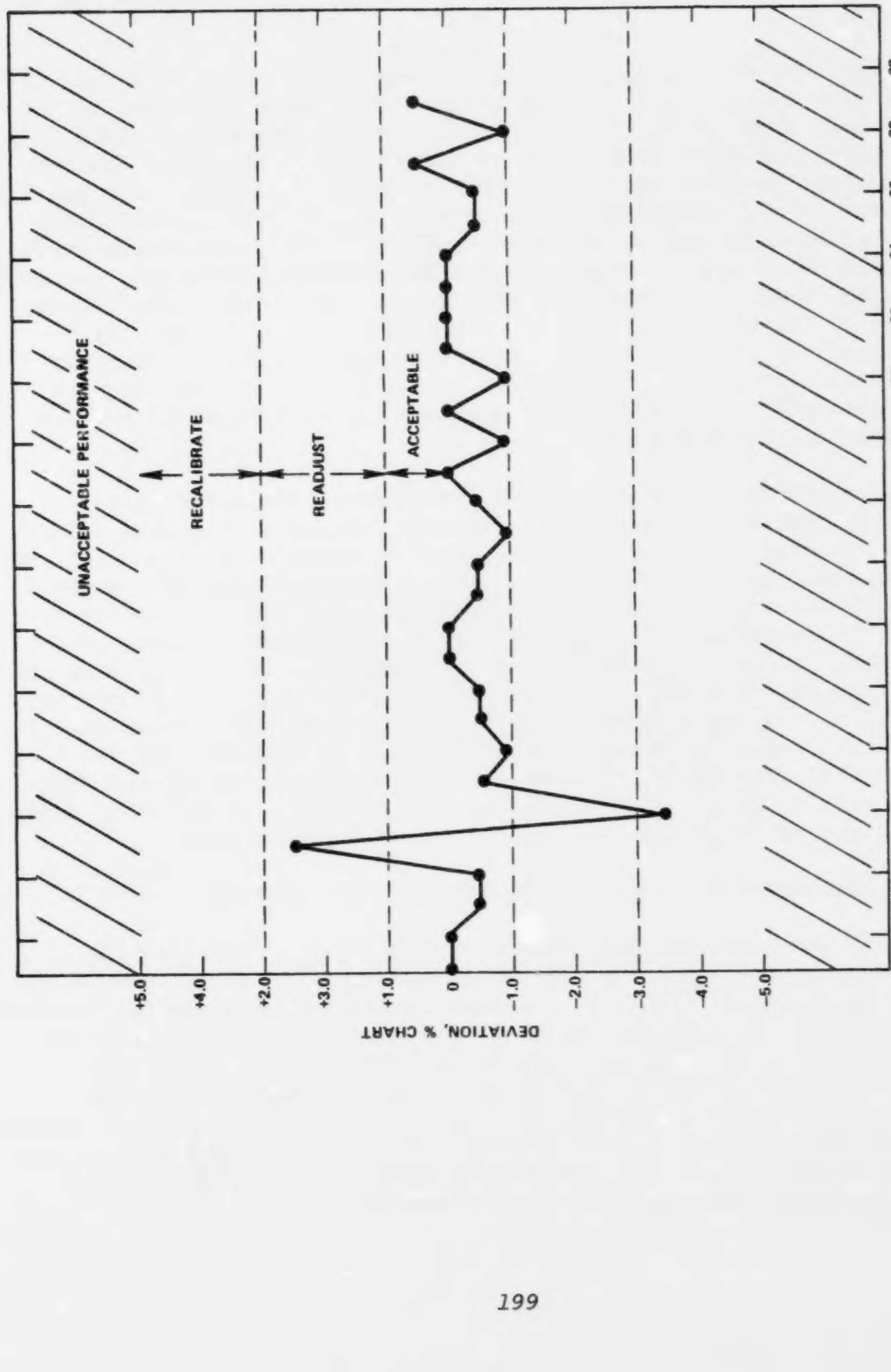


Figure 1. Typical zero drift for CO sampler.

positive displacement devices. The hi-vol and membrane samplers are calibrated with audit orifices. These orifices are calibrated using special Rootsmeters which have metric (m^3) scales readable to either 2 or 3 decimal places, depending on the flow range required. The hi-vols operate typically at 1.4 m^3/min, while the membrane samplers operate at 0.14 m^3/min. The dichotomous samplers because of their lower flow rate (14 ℓ/min fine channel and 0.4 ℓ/min coarse channel) must be calibrated against a dry-test meter or bubble flow tube.

Flow calibrations were scheduled on a monthly basis at the beginning of the study, but were dropped back to quarterly periods based on collected data. The data from these flow calibrations are processed by a Hewlett-Packard 9821 programmable calculator which has a plotter and printer. The audit devices such as the calibration orifices are calibrated in the laboratory, and plots with interpolated tables generated by the calculator. A typical membrane audit orifice calibration plot is shown in Figure 2. The programmable calculator has several advantages in a quality assurance program over hand processing of calibration data. This type of calculator: (1) standardizes formats and procedures, (2) eliminates errors in calculation, (3) utilizes statistically valid best fit procedures that are tedious by hand, (4) is faster, (5) generates an interpolated table to eliminate chart reading errors, and (6) allows technicians unfamiliar with fluid mechanics or statistics to provide the best possible calibration data.

One of the statistics generated by the calculator, the correlation coefficient R, is used to determine the degree of scatter of the data points about the best fit line. It was determined that an acceptance level could be established for each type of calibration, using a "typical" operator known to perform careful calibrations. Setting these limits provides a guideline for the technician to determine if his calibration is comparable to those generated in the past. If not, a recalibration is required. At present only the calibration of the hi-vol audit orifice using the Rootsmeter and the calibration of a hi-vol in the field with the audit orifice have correlation coefficient limits established. An R value of 0.9995 must be obtained for the 5-point orifice calibration and 0.9990 for the 5-point sampler calibration for these types of calibrations to be acceptable for the LACS. Coefficient acceptance limits for the other methods are currently being established.

LACS EXTERNAL SAMPLING QUALITY ASSURANCE PROGRAM

The need for audit checks performed by an individual other than the routine site operator and apparatus not associated with the study were recognized from the beginning of the LACS. Because of initial resource limitations and the confidence in the site operations by EPA operators, it was felt that a full scale external audit program could be omitted and only certain key aspects checked externally. After March, 1976, the site operations were turned over to the analysis contractor (Rockwell Air Monitoring Center), which began collection and analysis of LACS samples. An external audit program was then felt to be necessary to: (1) demonstrate comparability, (2) pinpoint problems, and (3) check the contractor's performance.

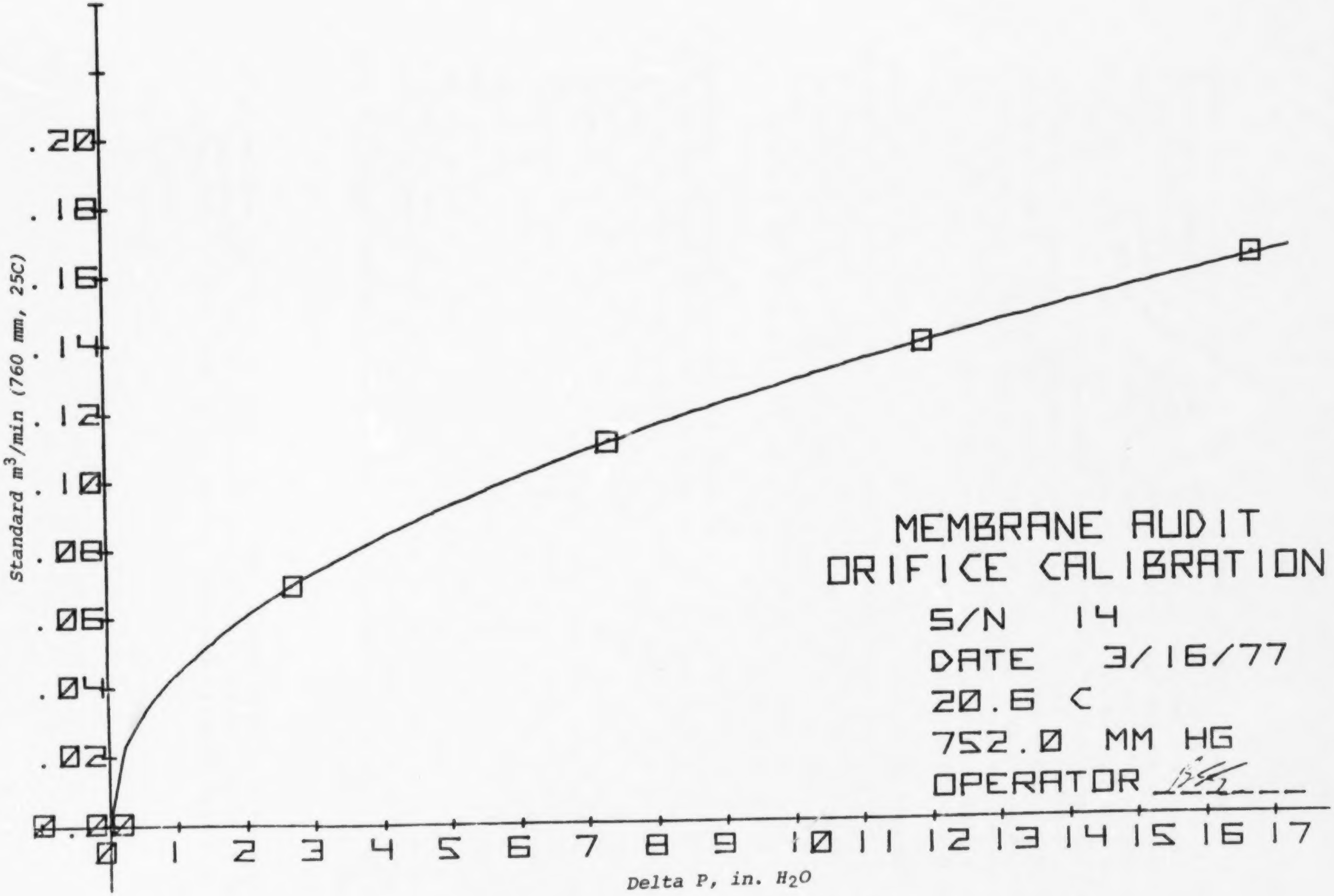


Figure 2. Sample calibration plot.

In December of 1976, an employee of EMB performed external audit checks (usually 2 span points) on all LACS samplers using test equipment and standards brought from Research Triangle Park, North Carolina. The continuous samplers were checked with span gas concentrations; the integrating samplers were checked for flowrate accuracy; and the flowmeters in the calibration systems also checked for flowrate accuracy. A comprehensive report was prepared listing the % differences and the number of samplers not operating within "acceptable limits." Table III is a summary of the results obtained from this external audit. Overall the results indicate generally acceptable operation of all LACS samplers as exhibited by the CO audit data in Figure 3. The two problem areas pinpointed were the somewhat poor performance of the Total Sulfur analyzer and the number of hi-vol and membrane sampler calibrations not falling within the "acceptance" limits.

The out-of-limits calibrations of the hi-vols and membrane samplers were readily traced to an inadvertent skipping of the previous quarterly hi-vol and membrane sampler calibration. Figure 4 is a sample plot of the hi-vol audit data. Although the average % differences were fortunately not substantial, the omission of the routine calibration is unacceptable, and a revised operations check sheet has been instituted along with provisions for periodic review by EPA personnel.

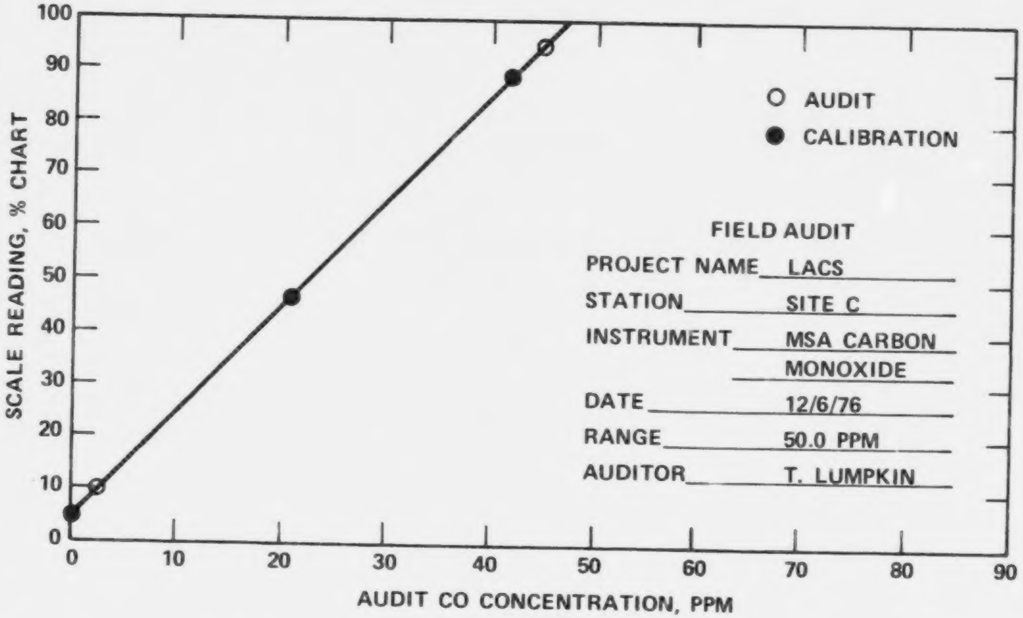
Except for the Total Sulfur analyzers, the continuous samplers performed extremely well as demonstrated by the typical CO audit plot shown in Figure 5. The Total Sulfur analyzers were expected to have a greater degree of variability during audit checks because of the very sensitive operational range (0.10 ppm full scale). However, examination of the comparison of the Total Sulfur monthly averages with those of the SO_2 bubblers operated at the same sites (see Figure 6) indicated that there were at times biases in one of the measurements. The line drawn through the data points represents the regression obtained in 1975, and all the points are within approximately ±8 $\mu g/m^3$ of this line except for those grouped above and below the line. These "outlier" points are all Site C values from 1976. Closer examination of the Total Sulfur sampler and associated calibrator at Site C resulted in the discovery of an intermittent leak in the calibrator assembly. This leak had apparently been causing problems all during the year, and was only discovered by exchanging the calibration system at Site C with that from Site A. This leak has since been corrected, but demonstrates that even with the best QA program some problems can still occur.

ACKNOWLEDGEMENT

The external audit data in this report were collected and compiled by Mr. Thomas A. Lumpkin of the Environmental Monitoring Branch, Environmental Monitoring and Support Laboratory, United States Environmental Protection Agency.

TABLE III. SUMMARY OF EXTERNAL AUDIT RESULTS

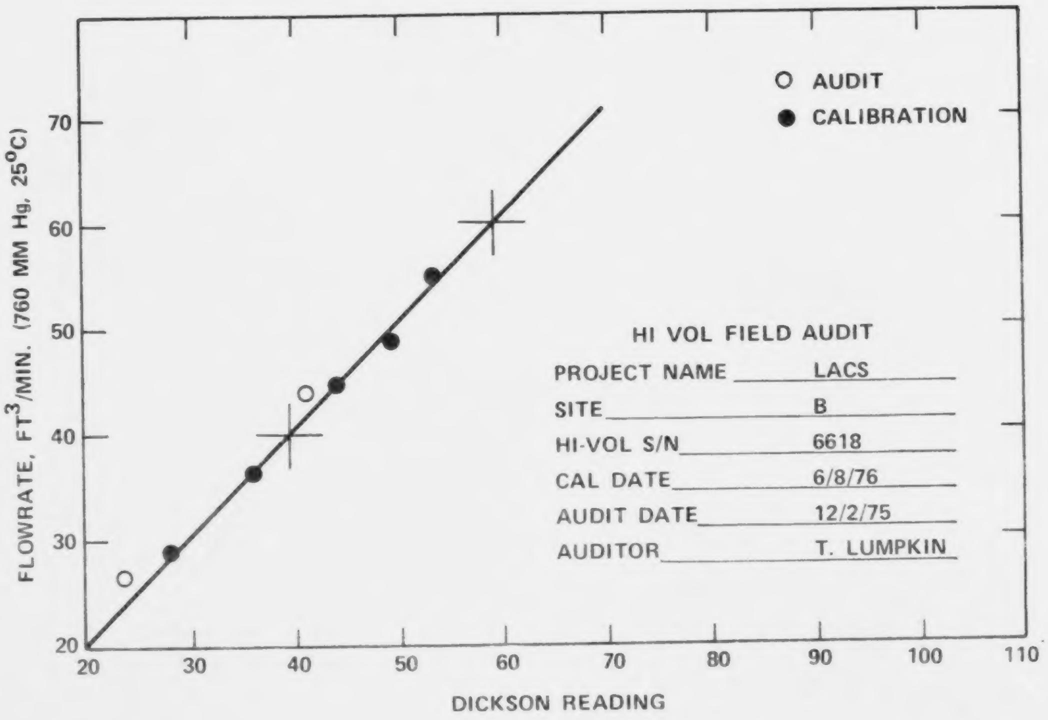
Instrument Audited	Number Audited	Number Operational	Audit Level	Acceptable Limits For Difference	Number Out-side Limits	Average Difference
Total Sulfur	2	2	0.06 ppm	± 0.009 ppm	1	- 0.009 ppm
Nitric Oxide	2	2	0.40 ppm	± 0.06 ppm	0	- 0.012 ppm
Nitrogen Dioxide	2	2	0.20 ppm	± 0.03 ppm	0	- 0.005 ppm
Ozone	2	2	0.20 ppm	± 0.03 ppm	0	- 0.007 ppm
Carbon Monoxide	2	2	20.0 ppm	± 3.0 ppm	0	0.28 ppm
Mass Flowmeters	10	10	2500 SCCM	± 125 SCCM	1	- 48 SCCM
High Volume Sampler Flow Rate	10	10	45 SCFM	± 10% of Audit Value	2	- 1.79 SCFM
Membrane/ Cascade Sampler Flow Rate	6	6	4 SCFM	± 10% of Audit Value	3	0.068 SCFM



FIELD AUDIT

PROJECT NAME LACS
STATION SITE C
INSTRUMENT MSA CARBON MONOXIDE
DATE 12/6/76
RANGE 50.0 PPM
AUDITOR T. LUMPKIN

Figure 3. Comparison of CO audit with last calibration.



HI VOL FIELD AUDIT

PROJECT NAME LACS

SITE B

HI-VOL S/N 6618

CAL DATE 6/8/76

AUDIT DATE 12/2/75

AUDITOR T. LUMPKIN

Figure 4. Comparison of hi vol audit with last calibration.

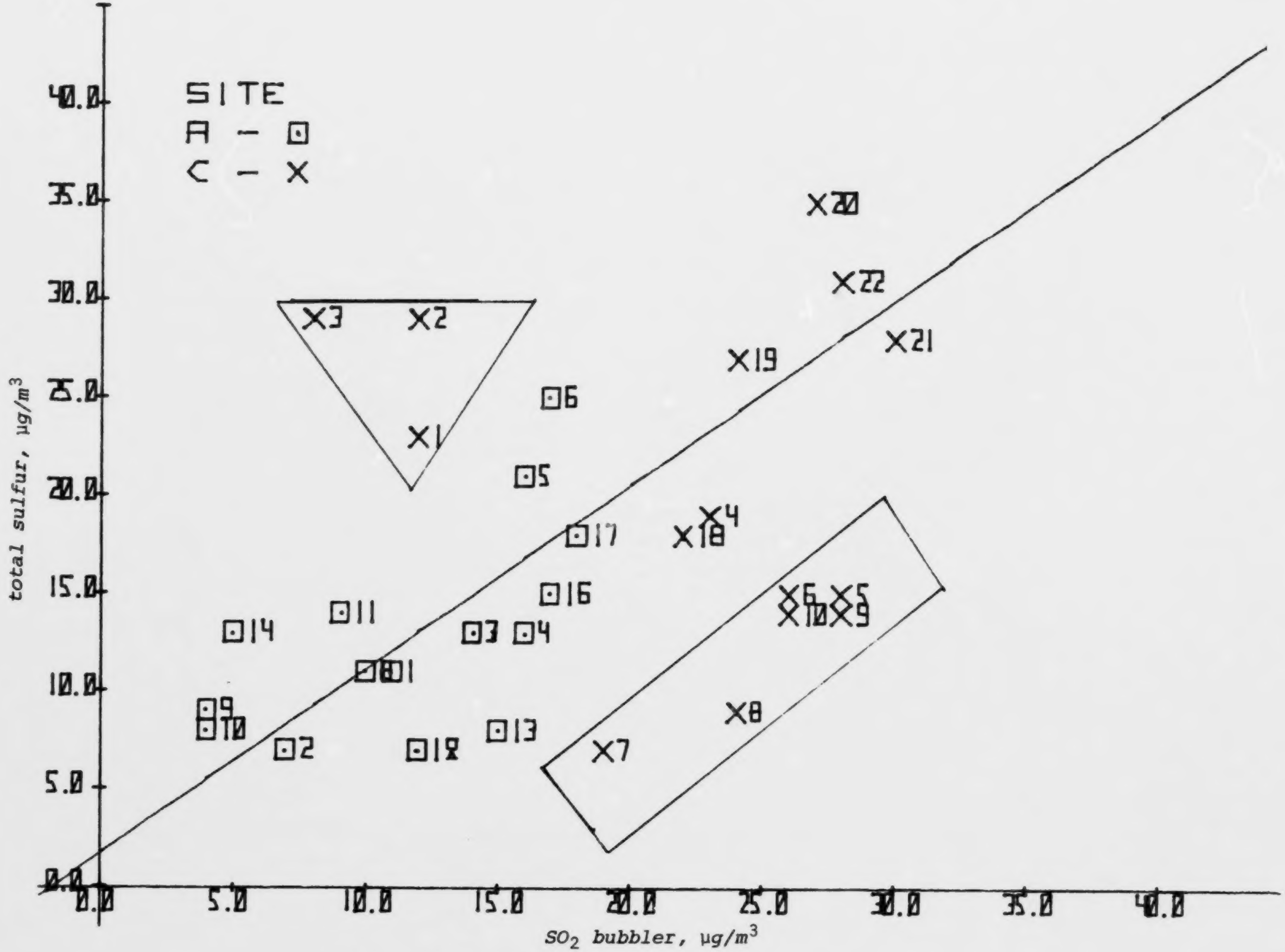


Figure 5. Comparison of monthly averages by site.

PRECISION OF LACS SAMPLING AND ANALYTICAL METHODS

Gary F. Evans

U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

Two special studies have been conducted at the Los Angeles Catalyst Study sites in an effort to identify and quantify the major sources of error inherent in the sampling and analytical methods employed.

First, co-located high volume samplers were operated concurrently for twelve 24-hour periods at a location 700 feet upwind from the freeway. Following equilibration and weighing, each exposed filter was analyzed in duplicate (using center and end strips) for concentrations of lead, ammonium ion, nitrate ion and sulfate ion by each of two laboratories. The results were used to construct estimates of the amount of variability (i.e., "variance component") between samplers, between laboratories and within laboratory. In addition, it was possible to investigate effects of strip position (center versus end) and the time lag between sample collection and chemical analysis on reported pollutant concentration.

The second study consisted of operating five samplers (two high volume samplers with glass fiber filters, two membrane samplers with cellulose ester filters and a single membrane sampler with teflon filters) at each of two sites (upwind and downwind) on a 4-hour interval (3-7 p.m.) for twelve days. In addition to final weight, each filter was analyzed in duplicate for sulfate ion concentration by each of two laboratories. Estimates were obtained for the between sampler, between laboratory and within laboratory components of variance. Finally, the effects of site and method on reported pollutant concentration were investigated.

INTRODUCTION

Two external quality assurance programs are being conducted in the Los Angeles Catalyst Study (LACS) to help measure and ensure the quality of data from the high volume (hi-vol) samplers operated at the sites. In the "split-sample" program, the analysis contractor, Rockwell Air Monitoring Center (RAMC), provides the referee laboratory, Environmental Monitoring and Support Laboratory (EMSL), with a strip from a representative sample of one to five percent of the total number of filters processed. The analyses obtained by the two laboratories for lead (Pb), ammonium ion (NH_4^+), nitrate ion (NO_3^-) and sulfate ion (SO_4=) are compared to provide some measure of the interlaboratory reproducibility for a given filter. In the "blindsample" program, each *laboratory is periodically provided with audit solutions of known concentrations for each of the pollutants of interest so that some measure of the accuracy of the analytical instruments used by each laboratory may be constructed. While these programs have produced much useful data, they are not sufficient in scope to establish the total variability of the monitoring system (including sampling) nor are they sufficiently comprehensive to allow the identification of the specific components of the monitoring system to which results are most sensitive (e.g., collection of samples, pre-conditioning of filters, cutting of strips, preparation of solutions, operation of analytical instruments, etc.).*

For these reasons, two short-term studies were designed and conducted at the LACS sites. The first involved hi-vol samplers operated on a 24-hour integrating period and was conducted in the summer of 1975. The second involved both hi-vol and membrane samplers operated on a 4-hour integrating period and was conducted in the summer of 1976.

TWENTY-FOUR HOUR HIGH VOLUME SAMPLER STUDY

PURPOSE

In the summer of 1975, a study involving 24-hour hi-vol samplers was designed and conducted at the site of the LACS freeway monitoring project to accomplish the following objectives:

- *To determine the variability inherent in the collection of samples by comparing the results of duplicate (i.e., co-located, simultaneoulsy operated) hi-vol samplers.*
- *To determine the between-laboratory variability in the analytical process by comparison of results from RAMC and EMSL (same filter).*
- *To determine the within-in laboratory variability in the analytical process by comparison of duplicate strips and instrument readings (same filter, same lab).*
- *To determine whether any general gradients in pollutant concentrations exist across the area of an exposed filter.*
- *To isolate those components of the monitoring system which give rise to the greatest amount of variability and which, should receive the greatest emphasis in future quality assurance efforts.*
- *To assess the quality of LACS data generated from hi-vol samplers [total suspended particulates (TSP), Pb, NH_4^+, NO_3^- and $SO_4^=$] by estimating the precision of the* total *monitoring system for each pollutant.*

EXPERIMENTAL DESIGN

A temporary site, designated A' and located 700 feet from the freeway on the upwind (ocean) side, was selected for this experiment (Figure 1). Site A'

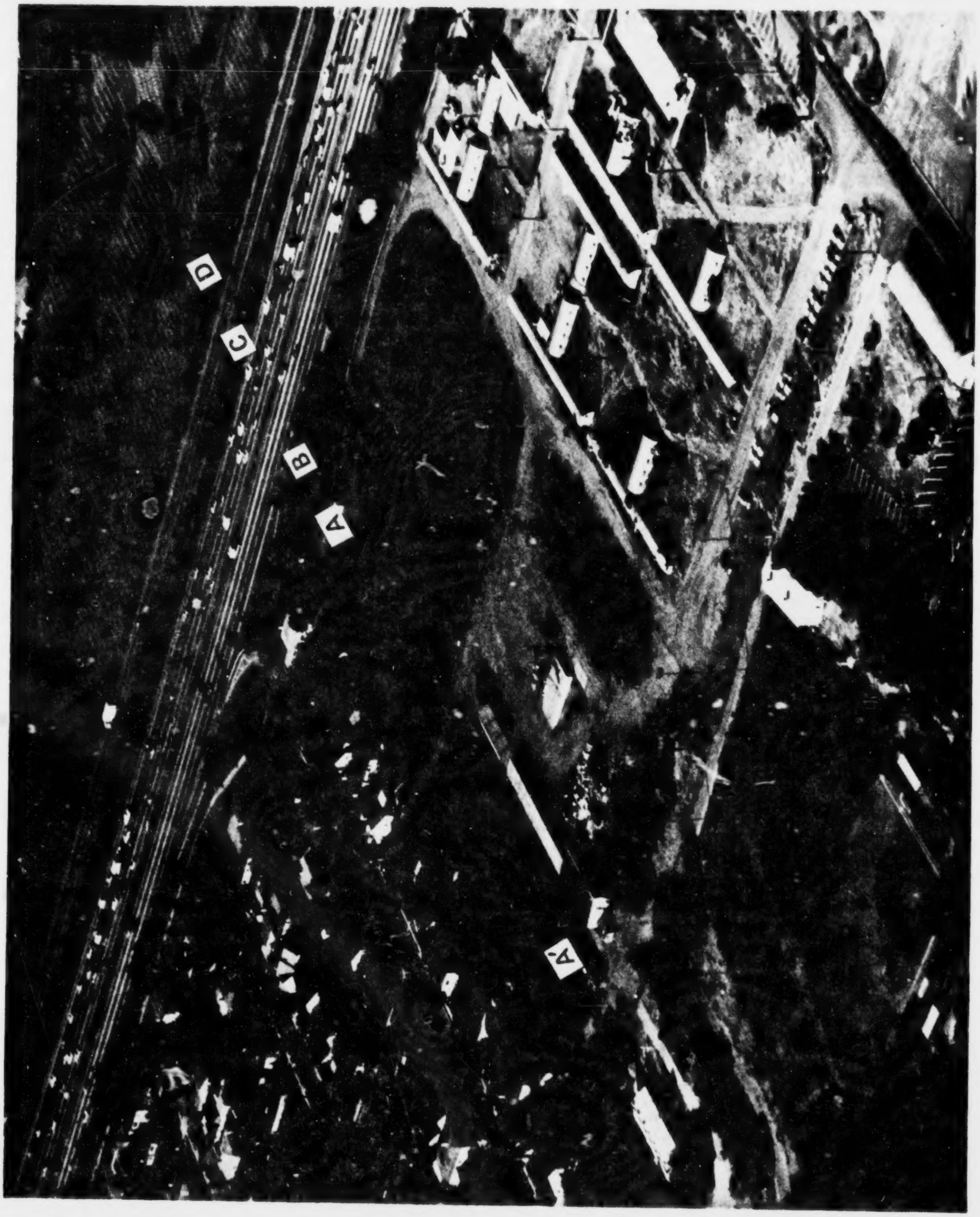


Figure 1. Aerial view of sampling sites.

was selected because it would theoretically be removed from the area in which concentration gradients exist for freeway-generated pollutants so that both samplers may be presumed to be exposed to the same (background) pollutant concentrations.

Two calibrated hi-vol samplers (designated #195 and #197, respectively) were placed side-by-side at the site and operated concurrently on a 24-hour (midnight-to-midnight) basis for a total of twelve days. The sampling days were not consecutive as that would have required the operation of samplers in tandem. The filters exposed during the first six sampling days were identified by date and sampler and delivered to RAMC for initial processing.

After equilibration and weighing, RAMC cut a pair of standard 3/4 inch strips from both sides of each filter and two pair of strips from the center (see Figure 2). Strip position was specified for two reasons. First, it was felt that maximum variability due to strips could be introduced into the experiment by requiring that duplicate strips be as far removed from each other as possible and secondly, by keeping track of the position from which a strip was cut, so it would later be possible to test whether the center of exposed filters tends to differ systematically in pollutant concentration from the ends of the filters. These four pairs of strips were assigned identification codes for the sampler (#195 or #197), analysis laboratory (RAMC or EMSL), strip position (center or end), and sampling date. The twenty-four pairs of strips designated EMSL were sent to EMSL for analysis.

Each laboratory prepared one member of each pair of strips for Pb analysis (by atomic absorption) and the other member for analysis of ammonium ion (by sodium phenolate), nitrate ion (by reduction-diazo coupling) and sulfate ion (by methylthymol blue (MTB) colorimetric). To the extent possible, each laboratory was requested to introduce these solutions into the stream of their routine analytical work, rather than to process them together as a batch.

The exposed filters from the final six days of sampling were sent to EMSL for initial processing (equilibration, weighing, cutting and identification of strips). These strips were then divided between the two laboratories and the chemical analyses were completed.

The experiment was designed to isolate each of three major components of the total monitoring system for Pb, NH_4^+, NO_3^- and $SO_4^=$ in order to determine whether and to what extent each component contributes to the variability in reported pollutant concentrations. The potential sources of variation considered are defined below:

(1) *Variation in Sample Collection -- Assuming that the two high volume samplers employed in the experiment were randomly selected from the infinite population of such samplers, the concentrations reported (averaged over laboratories and strips) may then be compared to test whether the samplers yielded results which were significantly different and, if so, to provide an estimate of the amount of variability (i.e., variance component) contributed by the factor "sampler."*

(2) *Variation Between Laboratories -- Similarly, assuming that the two*

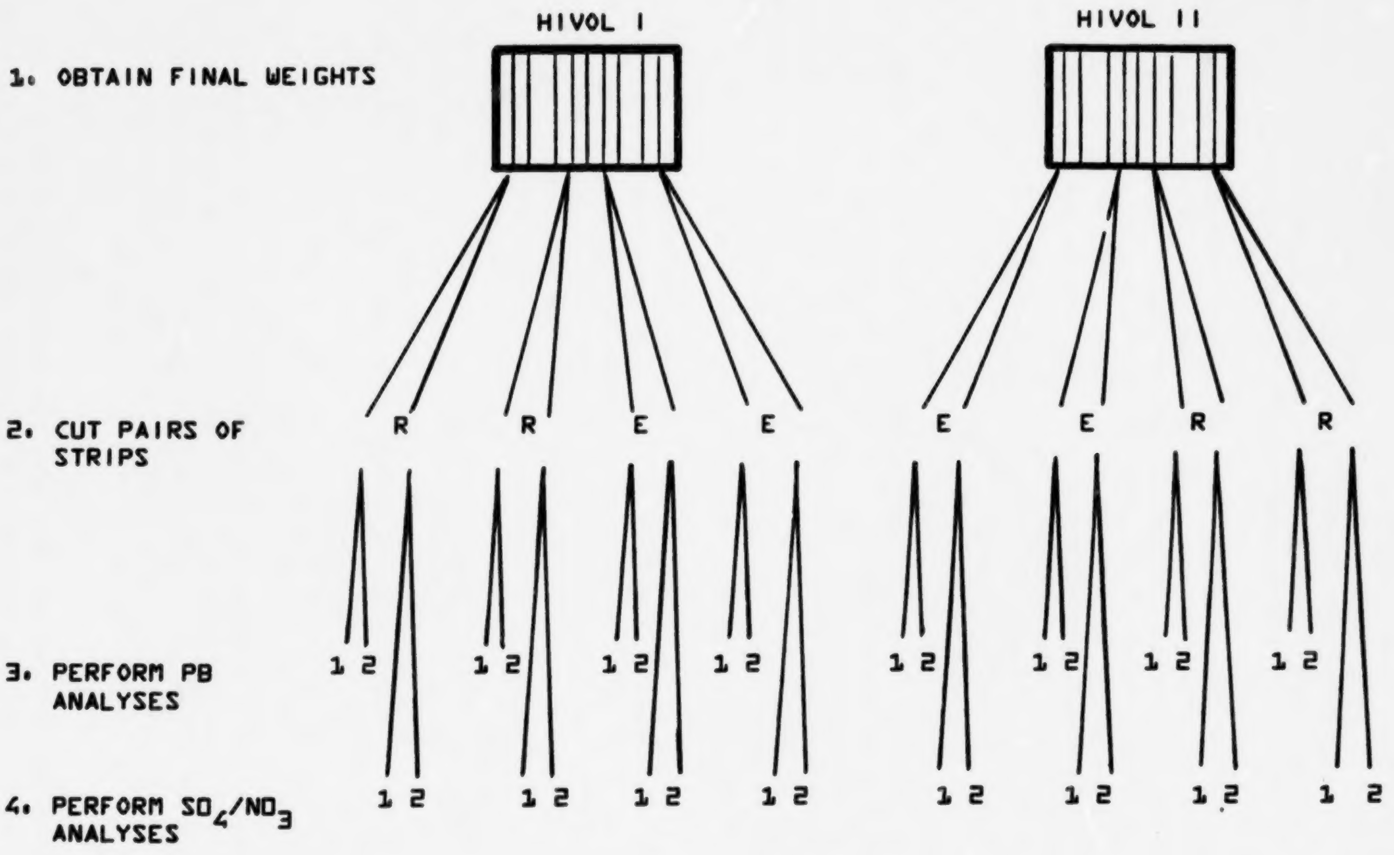

HIVOL I
HIVOL II
1. OBTAIN FINAL WEIGHTS
2. CUT PAIRS OF STRIPS
3. PERFORM PB ANALYSES
4. PERFORM SO_4/NO_3 ANALYSES
R
R
E
E
E
E
R
R
1 2
1 2
1 2
1 2
1 2
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Figure 2. Twenty-four hour study sample analysis.

laboratories employed in the experiment are a representative sample of the infinite population of such laboratories, the concentrations reported by laboratory (averaged over sampler and strips) may then be compared to test whether laboratories produced significantly different results and, if so, to provide an estimate of the variance component for the factor "laboratory."

(3) Variation Within Laboratory -- Since each laboratory processed two strips from each filter, it is possible to obtain an estimate of the variance component for the factor "strips" (within filter, within laboratory). This factor represents the variability contributed by all the analytical procedures conducted within a given laboratory (cutting strips, preparation of extraction solutions, and operation of analytical instrument). One laboratory (EMSL) also reported duplicate instrument readings for each of the extraction solutions prepared in the experiment. Using this data it is possible to obtain an estimate of the variance inherent in the analytical instrument itself. Within laboratory variance, then, may be subdivided into components for "strip preparation" (cutting and extraction) and "instrument reading."

The experiment is balanced in the sense that the dependent variable (measured pollutant concentration for a given 24-hour period) is uniformly exposed to two "crossed" independent variables (sampler and laboratory). Strip position may be considered a "nested" variable (within laboratory).

Because of the manner in which the experiment was designed and conducted, it was possible to evaluate the effects of two other potential sources of variation in the monitoring system. Since each laboratory processed a strip cut from the center and from the end of each filter (to insure maximum variability due to strip), a comparison was made of the results by strip position (averaged over sampler and laboratory) to determine whether center strips tended to differ from end strips in some systematic manner. Also, because one laboratory (RAMC) processed all the end strips from one set of filters approximately two months after they had processed the corresponding center strips, it was possible to evaluate whether the time lag between sampling and analysis date (within filter, within laboratory) had any impact on recorded concentrations.

DATA SUMMARY

Total suspended particulate data appear in Table I. As explained in the previous section, equilibration and final weighing were performed by RAMC for the first six days of the experiment and by EMSL for the final six days. It was not practical to have each laboratory obtain TSP values on the same filter, so that a direct determination of the effect of laboratories on TSP results is not available.

It is possible, however, to evaluate the effect of samplers. The percent difference between duplicate samplers is tabulated for each day and summarized by laboratory. The sampler differences are generally small (0.8% overall for RAMC and 3.6% overall for EMSL) and neither sampler produces results which are consistently higher than the other. A paired-t test was performed for each

TABLE I. DATA SUMMARY TSP ($\mu g/m^3$)

RAMC				EMSL			
Date	Sampler #195	Sampler #197	% Dif.[1]	Date	Sampler #195	Sampler #197	% Dif.[1]
6/04/75	76.0	76.8	-1.1	6/23/75	79.3	82.4	- 3.8
6/06/75	72.6	69.5	+4.4	7/03/75	105.0	107.4	- 2.3
6/08/75	62.3	63.1	-1.3	7/05/75	75.4	71.2	+ 5.7
6/10/75	89.3	87.1	+2.5	7/07/75	76.8	75.3	+ 2.0
6/12/75	76.6	77.2	-0.8	7/11/75	106.1	98.3	+ 7.6
6/16/75	74.8	74.5	+0.4	7/14/75	76.9	66.4	+14.7
Overall	75.3	74.7	+0.8		86.6	83.5	+ 3.6
Paired-t		+ 0.82 NS				+ 1.38 NS	
Corr. Coeff.		0.98				0.94	

1) $\% \text{ Dif.} = \frac{2(\#195 - \#197)}{\#195 + \#197} \times 100$

NS = Difference is not significant at P = 0.90

group (by laboratory) to determine whether or not the sampler differences were statistically significant once the variability due to date has been discounted. Since neither computed paired-t value was significant, we may conclude that no evidence appears in this data to suggest that sample collection introduces a bias in the determination of TSP concentration at the LACS sites.

Tables II through V contain the results obtained for Pb, NH_4^+, NO_3^-, and $SO_4^=$, respectively. For these pollutants, duplicate (end and center) results were reported by each laboratory for each of the duplicate samplers. Overall averages by sampler, laboratory, and strip position appear at the bottom of each table. Because the experimental design is balanced, these averages may be considered indicators of the magnitude of the effects produced by the independent variables in the experiment (i.e., sampler, laboratory and strip).

ANALYSIS OF VARIANCE

The statistical technique known as analysis of variance was applied to determine whether either samplers or laboratories were significant sources of variation in the data for Pb, NH_4^+, NO_3^- and $SO_4^=$. The data for each pollutant were treated as a 2x2 factorial experiment (samplers "crossed" with laboratories) conducted in twelve complete blocks (sampling days). For the purpose of this analysis, center and end strips results were considered as simply being within cell replicates.

The results of the four analyses of variance appear in Table VI. The significance of the F-values (right hand column) is denoted by asterisks. As would be expected, sampling date is a large source of variation and is significant in every case. Of much more interest, however, is the fact that sampler was not a significant source of variation for any of the four pollutants tested. Hence, as was the case with TSP, we may conclude that two properly calibrated hi-vol samplers operating side-by-side and concurrently will produce results which are statistically indistinguishable. Laboratory was a significant factor for Pb, NH_4^+ and NO_3^-, but not for $SO_4^=$.

VARIANCE COMPONENT

Using the mean square values obtained in the analysis of variance and considering the sampler and laboratory effects to be random rather than fixed, RAMC and EMSL are thought of as a random sample of an infinite poulation for possible analysis laboratories and samplers. Number 195 and number 197 are a random sample of an infinite population of possible high volume samplers. It is easy to obtain estimates of the variance in reported pollutant concentrations which is due to the sampler factor and the laboratory factor, respectively. The estimates of these "variance components" are obtained as follows.

$$\hat{\sigma}^2_{\text{Sampler}} = \frac{\text{Mean square due to samplers - Mean square error}}{48}$$

$$\hat{\sigma}^2_{\text{Lab}} = \frac{\text{Mean square due to laboratories - Mean square error}}{48}$$

TABLE II. DATA SUMMARY Pb ($\mu g/m^3$)

	Sampler #195				Sampler #197			
	RAMC		EMSL		RAMC		EMSL	
Date	End	Center	Center	End	End	Center	Center	End
6/04/75	0.70	0.90	0.94	0.95	0.80	0.80	0.86	0.93
6/06/75	0.30	0.60	0.55	0.52	0.40	0.40	0.51	0.45
6/08/75	0.50	0.60	0.57	0.55	0.50	0.60	0.56	0.58
6/10/75	0.70	0.60	0.73	0.76	0.70	0.50	0.52	0.64 E
6/12/75	0.70	0.60	0.70	0.56	1.00	0.70	0.70	0.71
6/16/75	0.70	0.60	0.68	0.67	0.70	0.60	0.79	0.72
6/23/75	0.40	0.50	0.69	0.66	0.50	0.60	0.65	0.69
7/03/75	3.40	3.70	3.80	3.74	3.60	2.90	3.55	3.33
7/05/75	2.70	3.00	3.38	3.40	3.00	2.70	1.51	3.09
7/07/75	2.10	2.70	2.47	2.34	2.50	2.40	4.50	4.75
7/11/75	2.70	2.70	3.08	2.86	2.50	2.30	2.67	2.44
7/14/75	0.60	0.20	0.62	0.58	0.60	0.40	0.46	0.50
Average	1.29	1.39	1.52	1.47	1.40	1.24	1.44	1.57

E = Estimated (Sample Lost)

OVERALL SAMPLER AVERAGES: #195 = 1.42, #197 = 1.41

OVERALL LAB AVERAGES : RAMC = 1.33, EMSL = 1.50

OVERALL STRIP AVERAGES : End = 1.43, Center = 1.40

TABLE III. DATA SUMMARY NH_4^+ ($\mu g/m^3$)

	Sampler #195				Sampler #197			
	RAMC		EMSL		RAMC		EMSL	
Date	End	Center	Center	End	End	Center	Center	End
6/04/75	0.63	1.63	0.30	0.10	0.61	1.45	0.30	0.20
6/06/75	1.04	2.19	0.70	0.70	1.08	2.22	0.80	0.60
6/08/75	1.33	2.32	0.90	0.80	1.31	2.32	1.00	0.80
6/10/75	1.76	2.64	1.30	1.30	2.04	2.63	1.50	1.50
6/12/75	1.80	2.59	1.40	1.60	1.93	2.71	1.40	1.50
6/16/75	2.07	3.10	1.80	1.70	2.31	3.13	1.70	1.80
6/23/75	1.97	1.97	1.60	1.50	1.88	1.91	1.10	1.40
7/03/75	0.76	0.78	0.50	0.30	0.72	0.89	0.30	0.50
7/05/75	0.41	0.42	0.50	0.00	0.40	0.42	0.20	0.20
7/07/75	0.27	0.29	0.00	0.00	0.24	0.29	0.30	0.30
7/11/75	1.03	1.06	0.50	0.50	0.84	0.95	0.50	0.90
7/14/75	0.78	0.80	0.50	0.50	0.79	0.78	0 40	0.40
Average	1.15	1.65	0.84	0.76	1.18	1.64	0.79	0.84

OVERALL SAMPLER AVERAGES: #195 = 1.10, #197 = 1.11

OVERALL LAB AVERAGES : RAMC = 1.41, EMSL = 0.81

OVERALL STRIP AVERAGES : End = 0.98, Center = 1.23

TABLE IV. DATA SUMMARY NO_3^- ($\mu g/m^3$)

	Sampler #195				Sampler #197			
	RAMC		EMSL		RAMC		EMSL	
Date	End	Center	Center	End	End	Center	Center	End
6/04/75	6.97	7.90	8.40	8.30	7.52	7.79	7.10	6.60
6/06/75	4.14	3.39	3.80	3.50	3.62	4.39	3.90	3.70
6/08/75	1.95	1.51	1.90	1.60	1.77	1.34	1.70	1.60
6/10/75	1.85	1.48	1.80	1.70	1.68	1.46	1.70	1.90
6/12/75	1.13	1.00	1.30	1.30	1.42	1.12	1.40	1.50
6/16/75	0.41	0.24	0.50	0.50	0.43	0.23	0.50	0.50
6/23/75	1.44	1.46	1.70	1.50	1.50	1.41	1.60	1.60
7/03/75	15.93	15.96	16.10	14.40	14.83	15.99	14.90	14.60
7/05/75	9.63	10.31	10.60	10.10	10.20	9.93	10.10	9.70
7/07/75	10.02	10.31	11.30	10.70	10.22	10.48	17.80	19.00
7/11/75	9.55	9.70	10.60	9.90	8.93	9.49	9.60	9.40
7/14/75	6.14	6.12	6.20	5.40	5.76	6.26	6.00	5.60
Average	5.76	5.78	6.18	5.74	5.66	5.82	6.36	6.31

OVERALL SAMPLER AVERAGES: #195 = 5.87, #197 = 6.04

OVERALL LAB AVERAGES : RAMC = 5.76, EMSL = 6.15

OVERALL STRIP AVERAGES : End = 5.87, Center = 6.04

TABLE V. DATA SUMMARY $SO_4^=$ ($\mu g/m^3$)

	Sampler #195				Sampler #197			
	RAMC		EMSL		RAMC		EMSL	
Date	End	Center	Center	End	End	Center	Center	End
6/04/75	12.5	14.5	13.3	12.2	14.0	14.5	13.6	12.6
6/06/75	14.2	16.2	15.4	14.9	14.4	16.1	15.3	14.5
6/08/75	18.2	20.4	19.6	17.6	18.6	20.4	19.7	18.2
6/10/75	22.5	24.8	22.7	22.5	24.4	24.4	23.5	24.9
6/12/75	24.1	25.4	23.8	24.7	23.5	24.9	24.6	25.3
6/16/75	24.3	25.7	27.5	26.8	26.2	26.4	24.1	26.0
6/23/75	23.6	24.3	23.9	23.3	23.9	24.6	23.2	22.9
7/03/75	13.9	14.0	14.8	13.3	14.7	14.7	14.0	13.8
7/05/75	10.0	10.3	10.4	10.2	9.9	10.0	10.0	9.8
7/07/75	8.9	9.1	9.3	8.4	9.8	9.8	17.1	18.1
7/11/75	17.2	16.9	16.3	16.3	14.1	14.7	14.8	14.3
7/14/75	17.4	18.1	17.5	16.6	14.8	15.4	14.2	14.2
Average	17.2	18.3	17.9	17.2	17.4	18.0	17.8	17.9

OVERALL SAMPLER AVERAGES: #195 = 17.7, #197 = 17.8

OVERALL LAB AVERAGES : RAMC = 17.7, EMSL = 17.7

OVERALL STRIP AVERAGES : End = 17.4, Center 18.0

TABLE VI. ANALYSIS OF VARIANCE

Pollutant	Source	D.F.	Sum of Squares	Mean Square	F-Value
Pb	Date	11	123.19591	11.19963	81.74688**
	Sampler	1	0.00036	0.00036	0.00265
	Lab	1	0.67683	0.67683	4.94024*
	Sampler x Lab	1	0.00873	0.00873	0.06371
	Error	80	10.96030	0.13700	
	Corrected Total	94	134.84213		
NH_4^+	Date	11	39.14085	3.55826	35.44556**
	Sampler	1	0.00540	0.00540	0.05379
	Lab	1	8.64000	8.64000	86.06729**
	Sampler x Lab	1	0.00094	0.00094	0.00934
	Error	81	8.13131	0.10039	
	Corrected Total	95	55.81850		
NO_3^-	Date	11	2217.33030	201.57548	161.64126**
	Sampler	1	0.68851	0.68851	0.55211
	Lab	1	3.67775	3.67775	2.94915*
	Sampler x Lab	1	0.97405	0.97405	0.78108
	Error	81	101.01143	1.24705	
	Corrected Total	95	2323.68204		
$SO_4^=$	Date	11	2653.80083	241.25462	110.43689**
	Sampler	1	0.26042	0.26042	0.11921
	Lab	1	0.00375	0.00375	0.00172
	Sampler x Lab	1	0.96000	0.96000	0.43945
	Error	1	176.94833	2.18455	
	Corrected Total	95	2831.97333		

* Source is significant at $p = 0.90$
**Source is significant at $p = 0.99$

It is also possible to obtain an estimate of the variance component for filters strips by means of the following equation:

$$\hat{\sigma}^2_{Strips} = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{2} (c_i - e_i)^2$$

where n = number of pairs of center and end strips

c_i = reported concentration center strip of pair i

e_i = reported concentration end strip of pair i

It should be noted that this estimate is apt to be on the conservative (high) side in this experiment since the position of the filter from which duplicate strips were cut was controlled (center and end) and since the estimate contains the variance due to the final step in the measurement process (analytical instrument reading).

As previously mentioned, one laboratory (EMSL) reported duplicate instrument readings for each of the extraction solutions prepared in the experiment These duplicate data appear in Table VII. Only the first value in each case was used in the data analyses which have been discussed. Using this duplicate data, however, it is possible to obtain an estimate of the variance inherent in the analytical instrument itself. This estimate is computed as follows:

$$\hat{\sigma}^2_{Within\ Instrument} = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{2} (R_{i1} - R_{i2})^2$$

where n = number of pairs of instrument readings

R_{i1} = 1st instrument reading for pair i

R_{i2} = 2nd instrument reading for pair i

The estimates of the variance components for these four factors (sampler, laboratory, strips and instrument readings) appear in Table VIII. Since only EMSL data were available for duplicate instrument readings and because RAMC data for duplicate strips are confounded with analysis data (see next Section), only EMSL data were used to estimate the variance components for strips and instrument readings. The estimate for strips was "corrected" by subtracting the corresponding estimate for readings. All of the data were used to estimate the variance components for samplers (zero for all pollutants) and laboratories (zero for $SO_4^=$ only).

The coefficient of variation ($CV = \frac{100 \times \text{standard deviation}}{\text{mean concentration}}$) *is shown in*

TABLE VII. DUPLICATE INSTRUMENT READINGS (EMSL)

	µg/m³			
Site	NH_4^+	NO_3^-	$SO_4^=$	Pb
195 Qc 6/04/75 (155) 7404257	0.3-0.5	8.4-8.3	13.3-13.5	0.94-0.92
195 Qe 6/04/75 (155) 7404257	0.1-0.1	8.3-8.0	12.2-12.3	0.95-0.95
197 Qe 6/04/75 (155) 7404258	0.2-0.2	6.6-6.4	12.6-12.7	0.93-0.92
197 Qc 6/04/75 (155) 7404258	0.3-0.3	7.1-7.1	13.6-13.7	0.86-0.84
195 Qe 6/06/75 (157) 7404273	0.7-0.6	3.5-3.4	14.9-14.9	0.52-0.55
195 Qc 6/06/75 (157) 7404273	0.7-0.7	3.8-3.6	15.5-15.1	0.55-0.55
197 Qe 6/06/75 (157) 7404272	0.6-0.6	3.7-3.6	14.5-14.5	0.45-0.46
197 Qc 6/06/75 (157) 7404272	0.8-0.7	3.9-3.9	15.3-15.5	0.51-0.53
195 Qe 6/08/75 (159) 7404290	0.8-0.8	1.6-1.6	17.6-17.7	0.55-0.56
195 Qc 6/08/75 (159) 7404290	0.9-0.9	1.9-1.8	19.6-19.6	0.57-0.57
197 Qe 6/08/75 (159) 7404291	0.8-0.8	1.6-1.5	18.2-18.2	0.58-0.58
197 Qc 6/08/75 (159) 7404291	1.0-1.0	1.7-1.7	19.7-19.7	0.56-0.56
195 Qe 6/10/75 (161) 7404164	1.3-1.3	1.7-1.6	22.5-22.5	0.76-0.76
195 Qc 6/10/75 (161) 7404164	1.3-1.3	1.8-1.7	22.7-21.7	0.73-0.73
197 Qe 6/10/75 (161) 7404163	1.5-1.4	1.9-1.8	24.9-24.6	lost
197 Qc 6/10/75 (161) 7404163	1.5-1.5	1.7-1.7	23.5-24.5	0.52-0.51
195 Qe 6/12/75 (163) 7404193	1.6-1.6	1.3-1.3	24.7-24.7	0.56-0.54
195 Qc 6/12/75 (163) 7404193	1.4-1.3	1.3-1.2	23.8-24.1	0.70-0.69
197 Qe 6/12/75 (163) 7404192	1.5-1.5	1.5-1.5	25.3-25.3	0.71-0.72
197 Qc 6/12/75 (163) 7404192	1.4-1.4	1.4-1.3	24.6-24.6	0.70-0.71
195 Qe 6/16/75 (167) 7404309	1.7-1.7	0.5-0.5	26.8-30.2	0.67-0.67
195 Qc 6/16/75 (167) 7404309	1.8-1.8	0.5-0.5	27.5-26.7	0.68-0.71
197 Qe 6/16/75 (167) 7404308	1.8-1.8	0.5-0.5	26.0-25.1	0.72-0.71
197 Qc 6/16/75 (167) 7404308	1.7-1.7	0.5-0.5	24.1-25.1	0.79-0.77
195 Qc 6/23/75 (174) 7404466	1.6-1.6	1.7-1.6	23.9-24.1	0.69-0.67
195 Qe 6/23/75 (174) 7404466	1.5-1.4	1.5-1.5	23.3-23.5	0.66-0.64
195 Qc 7/03/75 (184) 7404850	0.5-0.6	16.1-15.9	14.8-14.9	3.80-3.72
195 Qe 7/03/75 (184) 7404850	0.3-0.3	14.4-14.4	13.3-13.6	3.74-3.74
195 Qc 7/05/75 (186) 7404868	0.5-0.5	10.6-10.6	10.4-10.4	3.38-3.29
195 Qe 7/05/75 (186) 7404868	BMD-BMD	10.1-10.1	10.2- 9.8	3.40-3.29
195 Qc 7/07/75 (188) 7404425	BMD-BMD	11.3-11.0	9.3- 9.3	2.47-2.40
195 Qe 7/07/75 (188) 7404425	BMD-BMD	10.7-10.4	8.4- 8.7	2.34-2.29
195 Qc 7/11/75 (192) 7404889	0.5-0.5	10.6-10.2	16.3-16.4	3.08-3.00
195 Qe 7/11/75 (192) 7404889	0.5-0.5	9.9-9.7	16.3-16.4	2.86-2.79
195 Qc 7/14/75 (195) 7404549	0.5-0.4	6.2-5.9	17.5-17.5	0.62-0.62
195 Qe 7/14/75 (195) 7404549	0.5-0.5	5.4-5.2	16.6-16.5	0.58-0.60
197 Qe 6/23/75 (174) 7404465	1.4-1.4	1.6-1.6	22.9-22.9	0.69-0.68
197 Qc 6/23/75 (174) 7404465	1.1-1.1	1.6-1.6	23.2-23.0	0.65-0.64
197 Qe 7/03/75 (184) 7404849	0.5-0.5	14.6-14.6	13.8-13.8	3.33-3.28
197 Qc 7/03/75 (184) 7404849	0.3-0.3	14.9-14.9	14.0-14.0	3.55-3.50
197 Qe 7/05/75 (186) 7404869	0.2-0.2	9.7-9.8	9.8- 9.8	3.09-3.03
197 Qc 7/05/75 (186) 7404869	0.2-0.2	10.1-10.1	10.0-10.0	1.51-1.49
197 Qe 7/07/75 (188) 7404426	0.3-0.3	19.0-19.0	18.1-18.1	4.75-4.62
197 Qc 7/07/75 (188) 7404426	0.3-0.3	17.8-17.8	17.1-17.1	4.50-4.34
197 Qe 7/11/75 (192) 7404888	0.9-0.9	9.4-9.4	14.3-13.9	2.44-2.68
197 Qc 7/11/75 (192) 7404888	0.5-0.5	9.6-9.2	14.8-14.8	2.67-2.60
197 Qe 7/14/75 (195) 7404548	0.4-0.4	5.6-5.6	14.2-14.2	0.50-0.49
197 Qc 7/14/75 (195) 7404548	0.4-0.4	6.0-6.0	14.2-14.8	0.46-0.44

the table for each variance component and for the total variance (sum of the components) for each pollutant. This measure expresses the variance relative to concentration so that comparisons may be made. It is interesting to note, that, except in the case of NH_4^+ (where the variance due to laboratories is blown up by the confounding with analysis date), the largest source of variation in the total monitoring system for each pollutant is due to strips. Some of the variance between strips is undoubtedly due to real differences in concentration, but it seems probable that much of this strip-to-strip variability is introduced in the filter cutting and extraction processes. Perhaps strip preparation is a component of the high volume sampler monitoring system that should be given high priority in future method improvement and quality assurance efforts.

At the bottom of Table VIII, estimates of the variance in the measurement of TSP are given for each laboratory. These estimates were computed according to the following equation:

$$\hat{\sigma}^2_{TSP} = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{2} (S_{i1} - S_{i2})^2$$

where n = number of pairs of duplicate sampler results

S_{i1} = reported concentration for sampler #195

S_{i2} = reported concentration for sampler #197

Since the paired-t tests for samplers were not significant, this variance is interpreted to be error inherent in the equilibration and weighing processes rather than due to any real difference between duplicate samplers. As already discussed, a direct evaluation of the effect of laboratories on TSP measurement is not available, but a simple test may be applied to determine whether the variance in TSP measurement is consistent from laboratory to laboratory. This test consists of dividing the larger variance estimate by the smaller and comparing the quotient with the tabulated F-value at the appropriate degrees of freedom and confidence level. The test, shown at the bottom of Table VIII is positive in this case implying that measurement variance for TSP is indeed lab-dependent. It should be mentioned that the set of filters which was pre-processed by EMSL was mailed to North Carolina from Los Angeles and this may have introduced some variability. Since the lab factor doesn't enter into the computed variance estimates, they may be too small to represent the total monitoring system error. To partially compensate for this, the larger of the two estimates (CV=5.2%) should be considered the more realistic figure.

The coefficient of variation in the total monitoring system for four of the five pollutants are shown in bar graph format in Figure 3. The ammonium ion results are not included since, as explained in the next section, they were severly distorted by an unexpected effect due to the time lag between sample collection and chemical analysis.

TABLE VIII. ESTIMATES OF VARIANCE COMPONENTS $(\mu g/m^3)^2$

Variance Component	Pollutant							
	Pb		NH_4^+		NO_3^-		$SO_4^=$	
	$\hat{\sigma}^2$	CV*	$\hat{\sigma}^2$	CV*	$\hat{\sigma}^2$	CV*	$\hat{\sigma}^2$	CV*
Between Instrument Readings (within strips, filter, lab)	.00116	2.4%	.00125	3.2%	.01042	1.7%	.16823	2.3%
Between Strips (within filter, lab)	.05908	17.2%	.01542	11.2%	.13771	6.2%	.29927	3.1%
Between Labs (within filter)	.01128	7.5%	.17793	38.2%	.05071	3.8%	---	---
Between Samplers (duplicate hi-vols)	---	---	---	---	---	---	---	---
Overall	.07152	18.9%	.19460	39.9%	.19884	7.5%	.46750	3.9%

	RISC		EMSL	
	$\hat{\sigma}^2$	CV*	$\hat{\sigma}^2$	CV*
TSP	1.35	1.5%	17.20	5.2%

$$*CV = \frac{100\,\hat{\sigma}}{\bar{X}}$$

$$\hat{\sigma}^2\ (EMSL) \div \hat{\sigma}^2\ (RAMC) = 12.74 > F_{(6,6).01} = 8.47$$

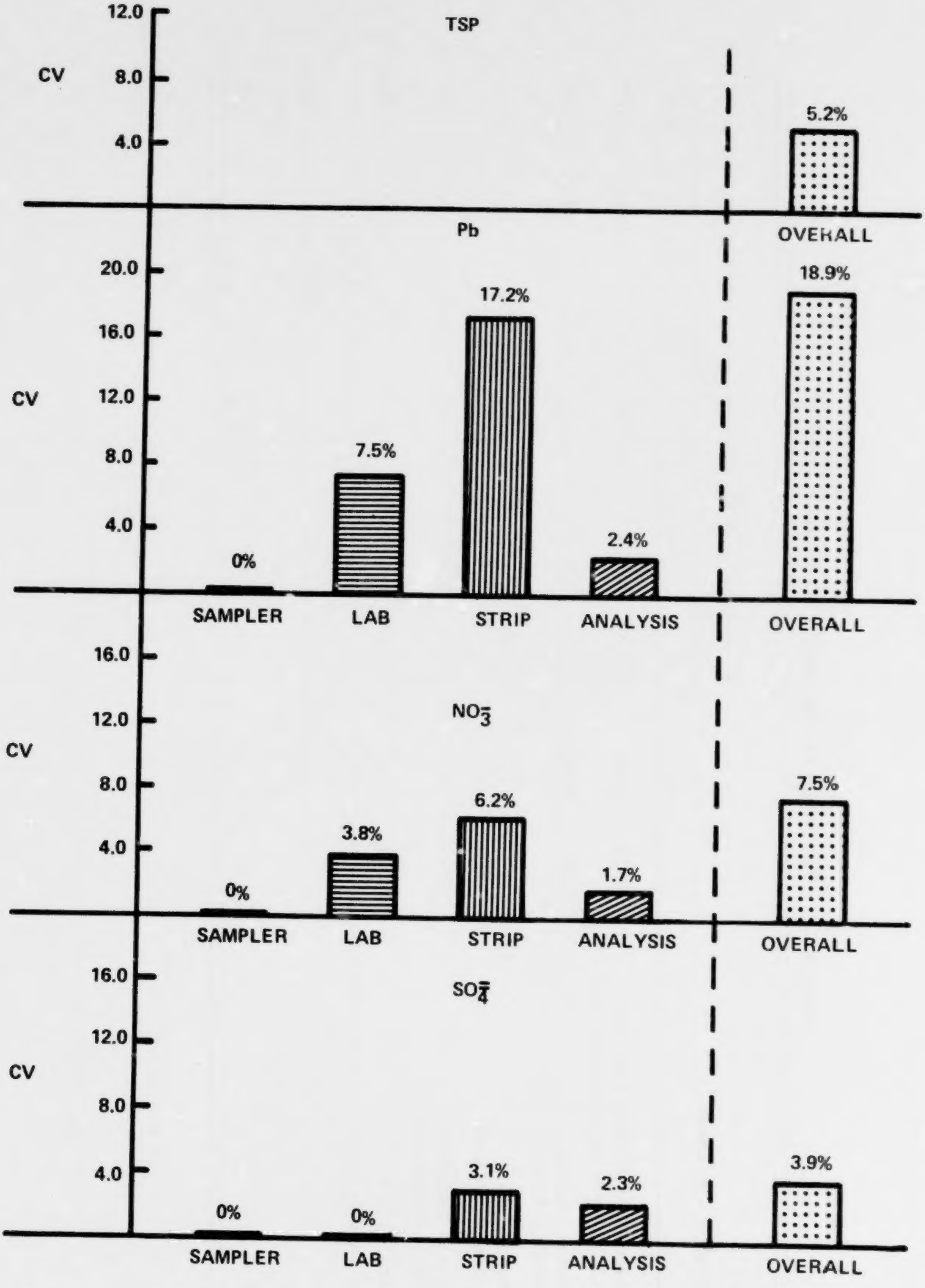

Figure 3. Twenty-four hour hi-vol. variance components $(CV=\frac{\hat{\sigma}}{\bar{x}}\cdot 100\%)$.

STRIP POSITION AND ANALYSIS DATE EFFECTS

In Tables IX though XII, the data for Pb, NH_4^+, NO_3^- and $SO_4^=$, respectively, are rearranged to facilitate an evaluation of the effect of strip position (center vs. end) on reported pollutant concentrations. The data in the tables are classified according to laboratory but not sampler since only the former appears to exert an influence on results.

The data are further classified into the first six and the final six sampling days of the study (designated sets I and II, respectively). This was done because "analysis date" (the date on which the chemical analysis of the sample was performed), though not originally intended to be a variable in the experiment, is apparently confounded (i.e., statistically inseparable) with strip position in the case of the RAMC analyses of the set I samples. The center strips from set I were all processed about two months earlier than the end strips making it impossible to know whether any differences between center and end strips were due to strip position effects, analysis date effects or both. This problem did not arise with the RAMC analyses for set II nor with any of the EMSL analyses. Hence, by observing the apparent strip position effect for the RAMC set I data in the context of the strip position behavior for the remaining data, it is possible to draw inferences about possible analysis date effects as well as strip position effects.

Once again, the paired-t statistic was used to test whether the differences in concentration between center and end strips are statistically significant. The test was performed for each of the four data subsets and also for the pooled data in which analysis date was not a confounding variable (RAMC set II and EMSL sets I and II).

The pattern of center vs. end differences for Pb appears to be random with mean zero for all of the data and none of the computed paired-t values are significant. One may conclude, therefore, that neither strip position nor analysis date have a significant bearing on Pb results.

The results for NH_4^+, however, are quite revealing. The RAMC data for set I center strips are considerably higher than the corresponding end strips (approximately 50 percent overall difference and a paired-t value which is significant with more than 99% probability). The remaining data (where possible analysis date effects are removed) exhibit a slight tendency for center strips to exceed end strips in concentration (about 4 percent overall difference with a paired-t value falling short of significance at the 95% probability level). Thus, it appears that while the center of a filter may be slightly higher in concentration than the ends, the time between sample collection and analysis is a much more critical factor in determining NH_4^+ concentrations. Apparently, NH_4^+ is lost during filter storage. This finding is consistent with the fact that the RAMC analysis for NH_4^+ has consistently been much higher than the EMSL analysis for the same filter in the split-sample program (RAMC performs its analysis several weeks before EMSL). It is interesting to note, however, the even the set II data in which both RAMC and EMSL performed their analyses on approximately the same date, the RAMC results are still a good deal higher than the corresponding EMSL results. Perhaps some difference exists between the filter storage environments in the two laboratories

TABLE IX. STRIP POSITION AND ANALYSIS DATE COMPARISONS
Pb ($\mu g/m^3$)

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/21/75	6/19/75	$\frac{2(c-e)}{c+e}$ x 100	8/28/75	8/28/75	$\frac{2(c-e)}{c+e}$ x 100
Set I		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/4/75	195	0.70	0.90	+ 25.0	0.94	0.95	- 1.1
	197	0.80	0.80	0.0	0.86	0.93	- 7.8
6/6/75	195	0.30	0.60	+ 66.7	0.55	0.52	+ 5.6
	197	0.40	0.40	0.0	0.51	0.45	+ 12.5
6/8/75	195	0.50	0.60	+ 18.2	0.57	0.55	+ 3.6
	197	0.50	0.60	+ 18.2	0.56	0.58	- 3.5
6/10/75	195	0.70	0.60	- 15.4	0.73	0.76	- 4.0
	197	0.70	0.50	- 33.3	0.52	Lost	---
6/12/75	195	0.70	0.60	- 15.4	0.70	0.56	+ 22.2
	197	1.00	0.70	- 35.3	0.70	0.71	- 1.4
6/16/75	195	0.70	0.60	- 15.4	0.68	0.67	+ 1.5
	197	0.70	0.60	- 15.4	0.79	0.72	+ 9.3
Overall		0.64	0.63	- 1.6	0.69	0.67	+ 2.9
Paired-t			-0.34			+1.00	
Corr. Coeff.			0.48			0.94	

continued

TABLE IX. CONTINUED

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/27/75	8/27/75	$\frac{2(c-e)}{c+e} \times 100$	8/28/75	8/28/75	$\frac{2(c-e)}{c+e} \times 100$
Set II		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/23/75	195	0.40	0.50	+ 22.2	0.69	0.66	+ 4.4
	197	0.50	0.60	+ 18.2	0.65	0.69	- 6.0
7/3/75	195	3.40	3.70	+ 8.5	3.80	3.74	+ 1.6
	197	3.60	2.90	- 21.5	3.55	3.33	+ 6.4
7/5/75	195	2.70	3.00	+ 10.5	3.38	3.40	- 0.6
	197	3.00	2.70	- 10.5	1.51	3.09	- 68.7
7/7/75	195	2.10	2.70	+ 25.0	2.47	2.34	+ 5.4
	197	2.50	2.40	- 4.1	4.50	4.75	- 5.4
7/11/75	195	2.70	2.70	0.0	3.08	2.86	+ 7.4
	197	2.50	2.30	- 8.3	2.67	2.44	+ 9.0
7/14/77	195	0.60	0.20	-100.0	0.62	0.58	+ 6.7
	197	0.60	0.40	- 40.0	0.46	0.50	- 8.3
Overall		2.05	2.01	- 2.0	2.28	2.37	- 3.9
Paired-t			-0.41			-0.59	
Corr. Coeff.			0.96			0.94	
				Center Avg.	End Avg.	%Dif.	Paired-t
Pooled Data (excluding RAMC-Set I)				1.69	1.73	-2.3	-0.64

* Difference is significant at P = 0.95

**Difference is significant at P = 0.99

TABLE X. CONTINUED

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/25/75	8/25/75	$\frac{2(c-e)}{c+e} \times 100$	8/22/75	8/22/75	$\frac{2(c-e)}{c+e} \times 100$
Set II		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/23/75	195	1.97	1.97	0.0	1.60	1.50	+ 6.5
	197	1.88	1.91	+ 1.6	1.10	1.40	- 24.0
7/3/75	195	0.76	0.78	+ 2.6	0.50	0.30	+ 50.0
	197	0.72	0.89	+ 21.1	0.30	0.50	- 50.0
7/5/75	195	0.41	0.42	+ 2.4	0.50	0.00	+200.0
	197	0.40	0.42	+ 4.9	0.20	0.20	0.0
7/7/75	195	0.27	0.29	+ 7.1	0.00	0.00	0.0
	197	0.24	0.29	+ 18.9	0.30	0.30	0.0
7/11/75	195	1.03	1.06	+ 2.9	0.50	0.50	0.0
	197	0.84	0.95	+ 12.3	0.50	0.90	- 57.1
7/14/75	195	0.78	0.80	+ 2.5	0.50	0.50	0.0
	197	0.79	0.78	- 1.3	0.40	0.40	0.0
Overall		0.84	0.88	+ 4.7	0.53	0.54	- 1.9
Paired-t			+2.66*			-0.12	
Corr. Coef.			0.99			0.88	
				Center Avg.	End Avg.	%Dif.	Paired-t
Pooled Data (excluding RAMC-Set I)				0.84	0.81	+3.6	+1.56

* Difference is significant at P = 0.95
**Difference is significant at P = 0.99

TABLE X. STRIP POSITION AND ANALYSIS DATE COMPARISONS
NH_4^+ ($\mu g/m^3$)

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/15/75	6/16/75	$\frac{2(c-e)}{c+e} \times 100$	8/21/75	8/21/75	$\frac{2(c-e)}{c+e} \times 100$
Set I		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/4/75	195	0.63	1.63	+ 88.5	0.30	0.10	+100.0
	197	0.61	1.45	+ 81.6	0.30	0.20	+ 40.0
6/6/75	195	1.04	2.19	+ 71.2	0.70	0.70	0.0
	197	1.08	2.22	+ 69.1	0.80	0.60	+ 28.6
6/8/75	195	1.33	2.32	+ 54.3	0.90	0.80	+ 11.8
	197	1.31	2.32	+ 55.7	1.00	0.80	+ 22.2
6/10/75	195	1.76	2.64	+ 40.0	1.30	1.30	0.0
	197	2.04	2.63	+ 25.3	1.50	1.50	0.0
6/12/75	195	1.80	2.59	+ 40.0	1.40	1.60	- 13.3
	197	1.93	2.71	+ 33.6	1.40	1.50	- 6.9
6/16/75	195	2.07	3.10	+ 39.9	1.80	1.70	+ 5.7
	197	2.31	3.13	+ 30.2	1.70	1.80	- 5.7
Overall		1.49	2.41	+ 47.2	1.09	1.05	+ 3.7
Paired-t			19.40**			+1.10	
Corr. Coeff.		0.96				0.98	

continued

TABLE XI. STRIP POSITION AND ANALYSIS DATE COMPARISONS
NO_3^- ($\mu g/m^3$)

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/15/75	6/16/75	$\frac{2(c-e)}{c+e} \times 100$	8/21/75	8/21/75	$\frac{2(c-e)}{c+e} \times 100$
Set I		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/4/75	195	6.97	7.90	+ 12.5	8.40	8.30	+ 1.2
	197	7.52	7.79	+ 3.5	7.10	6.60	+ 7.3
6/6/75	195	4.14	3.39	- 19.9	3.80	3.50	+ 8.2
	197	3.62	4.39	+ 19.2	3.90	3.70	+ 5.3
6/8/75	195	1.95	1.51	- 25.4	1.90	1.60	+ 17.1
	197	1.77	1.34	- 27.7	1.70	1.60	+ 6.1
6/10/75	195	1.85	1.48	- 22.2	1.80	1.70	+ 5.7
	197	1.68	1.46	- 14.0	1.70	1.90	- 11.1
6/12/75	195	1.13	1.00	- 12.2	1.30	1.30	0.0
	197	1.42	1.12	- 23.6	1.40	1.50	- 6.9
6/16/75	195	0.41	0.24	- 52.3	0.50	0.50	0.0
	197	0.43	0.23	- 60.6	0.50	0.50	0.0
Overall		2.74	2.65	- 3.3	2.83	2.73	+ 3.6
Paired-t			-0.60			+1.95	
Corr. Coef.			0.99			0.99	

continued

TABLE XI. CONTINUED

Set II		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/25/57	8/25/75	$\frac{2(c-e)}{c+e} \times 100$	8/22/75	8/22/75	$\frac{2(c-e)}{c+e} \times 100$
		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/23/75	195	1.44	1.46	+ 1.4	1.70	1.50	+ 12.5
	197	1.50	1.41	- 6.2	1.60	1.60	0.0
7/3/75	195	15.93	15.96	+ 0.2	16.10	14.40	+ 11.2
	197	14.83	15.99	+ 7.5	14.90	14.60	+ 2.0
7/5/75	195	9.63	10.31	+ 6.8	10.60	10.10	+ 4.8
	197	10.20	9.93	- 2.7	10.10	9.70	+ 4.0
7/7/75	195	10.02	10.31	+ 2.9	11.30	10.70	+ 5.5
	197	10.22	10.48	+ 2.5	17.80	19.00	- 6.5
7/11/75	195	9.55	9.70	+ 1.6	10.60	9.90	+ 6.8
	197	8.93	9.49	+ 6.1	9.60	9.40	+ 2.1
7/14/75	195	6.14	6.12	- 0.3	6.20	5.40	+ 13.8
	197	5.76	6.26	+ 8.3	6.00	5.60	+ 6.9
Overall		8.68	8.95	+ 3.1	9.71	9.33	+ 4.0
Paired-t			+2.38*			+2.01	
Corr. Coef.			0.99			0.99	
				Center Avg.	End Avg.	% Dif.	Paired-t
Pooled Data (excluding RAMC-Set I)				7.16	6.91	+3.6	+3.32**

* Difference is significant at $P = 0.95$
**Difference is significant at $P = 0.99$

TABLE XII. STRIP POSITION AND ANALYSIS DATE COMPARISONS

$SO_4^{=}$ ($\mu g/m^3$)

Set I		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/15/75	6/16/75	$\frac{2(c-e)}{c+e} \times 100$	8/21/75	8/21/75	$\frac{2(c-e)}{c+e} \times 100$
		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/4/75	195	12.5	14.5	+ 14.8	13.3	12.2	+ 8.6
	197	14.0	14.5	+ 3.5	13.6	12.6	+ 7.6
6/6/75	195	14.2	16.2	+ 13.2	15.4	14.9	+ 3.3
	197	14.4	16.1	+ 11.2	15.3	14.5	+ 5.4
6/8/75	195	18.2	20.4	+ 11.4	19.6	17.6	+ 10.8
	197	18.6	20.4	+ 9.3	19.7	18.2	+ 7.2
6/10/75	195	22.5	24.8	+ 9.7	22.7	22.5	+ 0.9
	197	24.4	24.4	0.0	23.5	24.9	- 5.8
6/12/75	195	24.1	25.4	+ 5.3	23.8	24.7	- 3.7
	197	23.5	24.9	+ 5.8	24.6	25.3	- 2.8
6/16/75	195	24.3	25.7	+ 5.6	27.5	26.8	+ 2.6
	197	26.2	26.4	+ 0.8	24.1	26.0	- 7.6
Overall		19.7	21.0	+ 6.4	20.3	20.0	+ 1.5
Paired-t			+ 6.24**			+ 0.69	
Corr. Coef.			0.97			0.98	

continued

TABLE XII. CONTINUED

		RAMC			EMSL		
		Analysis Date			Analysis Date		
		8/25/75	8/25/75	$\frac{2(c-e)}{c+e} \times 100$	8/22/75	8/22/75	$\frac{2(c-e)}{c+e} \times 100$
Set II		End	Center	%Dif.	Center	End	%Dif.
Sample Date	Sampler						
6/23/75	195	23.6	24.3	+ 2.9	23.9	23.3	+ 2.5
	197	23.9	24.6	+ 2.9	23.2	22.9	+ 1.3
7/3/75	195	13.9	14.0	+ 0.7	14.8	13.3	+ 10.7
	197	14.7	14.7	0.0	14.0	13.8	+ 1.4
7/5/75	195	10.0	10.3	+ 3.0	10.4	10.2	+ 1.9
	197	9.9	10.0	+ 1.0	10.0	9.8	+ 2.0
7/7/75	195	8.9	9.1	+ 2.2	9.3	8.4	+ 10.2
	197	9.8	9.8	0.0	17.1	18.1	- 5.7
7/11/75	195	17.2	16.9	- 1.8	16.3	16.3	0.0
	197	14.1	14.7	+ 4.2	14.8	14.3	+ 3.4
7/14/75	195	17.4	18.1	+ 3.9	17.5	16.6	+ 5.3
	197	14.8	15.4	+ 4.0	14.2	14.2	0.0
Overall		14.9	15.2	+ 2.0	15.5	15.1	+ 2.6
Paired-t			+ 3.12**			+ 2.02	
Corr. Coef.			0.99			0.99	
				Center Avg.	End Avg.	% Dif.	Paired-t
Pooled Data (excluding RAMC-Set I)				17.0	16.7	+1.8	+2.31*

* Difference is significant at P = 0.95
**Difference is significant at P = 0.99

which affects NH_4^+ loss or perhaps there are some differences in the way the analysis method is applied in the two laboratories which accounts for this difference. At any rate, it is suggested that further experimentation be conducted to substantiate NH_4^+ loss on storage and interlaboratory differences in the sodium phenolate method for NH_4^+ analysis.

For the NO_3^- data in which analysis date is not a factor (RAMC set II, EMSL set I and II), center strips showed a tendency to exceed end strips (about 4 percent overall difference with a paired-t value which is significant at the 99% confidence level). Although the RAMC set I data appears to run counter to this pattern (later analyzed strips exceeding earlier analyzed strips), the paired-t value was not significant so that no conclusion about analysis date effect may be drawn.

The pooled $SO_4^=$ data (excluding RAMC set I) showed a strip position effect similar to that for NH_4^+ and NO_3^- (about 2 percent overall difference, significant at the 95% probability level). The RAMC set I data for $SO_4^=$ suggests that lag time between sampling and analysis has increased the center vs. end differences (about 6 percent overall difference with more than 99% probability of significance). It is possible that some $SO_4^=$ loss occurs during filter storage, but it is apparently a much less serious problem than with NH_4^+.

FOUR-HOUR HIGH VOLUME AND MEMBRANE SAMPLER STUDY

PURPOSE

High volume and membrane samplers are operated for a 4-hour integrating period (3-7 p.m.) at the LACS sites because this period is characterized by maximum diurnal traffic density and wind directions (seabreeze) which are favorable to the detection of the freeway contribution to ambient pollutant concentrations.

In the summer of 1976, a study was undertaken to provide estimates of the variances associated with the components of 4-hour particulate sampling and subsequent analysis for $SO_4^=$ using both high volume and membrane samplers. By combining the precision tests for the two sampling methods into a single concurrent experiment, a secondary objective of obtaining data useful for establishing inter-method comparability was accomplished at little additional expense. Also, conducting the study simultaneously at site A (100' upwind) and site C (25' downwind) provided a test of the cross-freeway difference in pollutant concentration and method precision.

The objectives of the study, then, were to provide information concerning the following:

(1) 4-Hour Hi-Vol Precision. To estimate the between sampler, between laboratory and within laboratory components of variance for particulate sampling and subsequent $SO_4^=$ analysis using hi-vol samplers from 3-7 p.m. at the LACS sites.

(2) 4-Hour Membrane Precision. To estimate the between sampler, between laboratory and within laboratory components of variance for particulate sampling and subsequent $SO_4^=$ analysis using membrane samplers from 3-7 p.m. at the LACS sites.

(3) Method Comparability. To determine the extent of agreement in concentration level and measurement precision between samples collected by hi-vol and membrane samplers operated on a 4-hour basis at the LACS sites and analyzed for TSP and $SO_4^=$.

(4) Site Comparability. To determine what differences exist in concentration level and measurement precision between LACS sites A and C for TSP and $SO_4^=$ for the 3-7 p.m. sampling interval.

EXPERIMENTAL DESIGN

The placement of samplers for the study is shown in Figure 4. A pair of hi-vol samplers using glass fiber filters, a pair of membrane filters using cellulose ester filters, and a single membrane sampler using teflon filters were placed at each of the two sites (A and C). Though not routinely used in the LACS, the teflon filters were included in the study as a control since both glass fiber and cellulose ester filters are suspected of being subject to an artifact $SO_4^=$ formation (via SO_2 conversion on the filter media). The ten samplers were operated from 3-7 p.m. for twelve days. As indicated in Figure 4, the prevailing wind direction was perpendicular to the freeway (from site A toward site C) from 3-7 p.m. during each day of the study.

The cutting and assignment of filter partitions is illustrated in Figure 5. Once again, one center and one end strip from each glass fiber filter were assigned to each of the participating laboratories (RAMC and EMSL). Since chemical analysis did not appear to be a large source of variation in the 24-hour hi-vol study, the laboratories reported a single analysis per strip in this study. Membrane filters (102 mm in diameter) are much smaller in area than glass fiber filters (8 in. x 10 in.) and cannot be partitioned further than quarters for chemical extraction and analysis. Thus, $SO_4^=$ was the only pollutant determined other than TSP. Diagonal quarters from each membrane filter were assigned to each of the laboratories for a single $SO_4^=$ determination.

DATA SUMMARY

The study results are presented by method, site and pollutant in Tables XIII through XXIV. Again, paired-t tests were computed to determine whether any statistically significant biases in TSP concentration exist between a pair of samplers of the same type and operated at the same location. No such biases were found. Overall averages by sampler, laboratory and strip position appear at the bottom of each table of $SO_4^=$ results.

ANALYSIS OF VARIANCE

For purposes of analysis, the $SO_4^=$ data was first considered to consist of four subsets, classified by sampling method and site, as shown in Table 25.

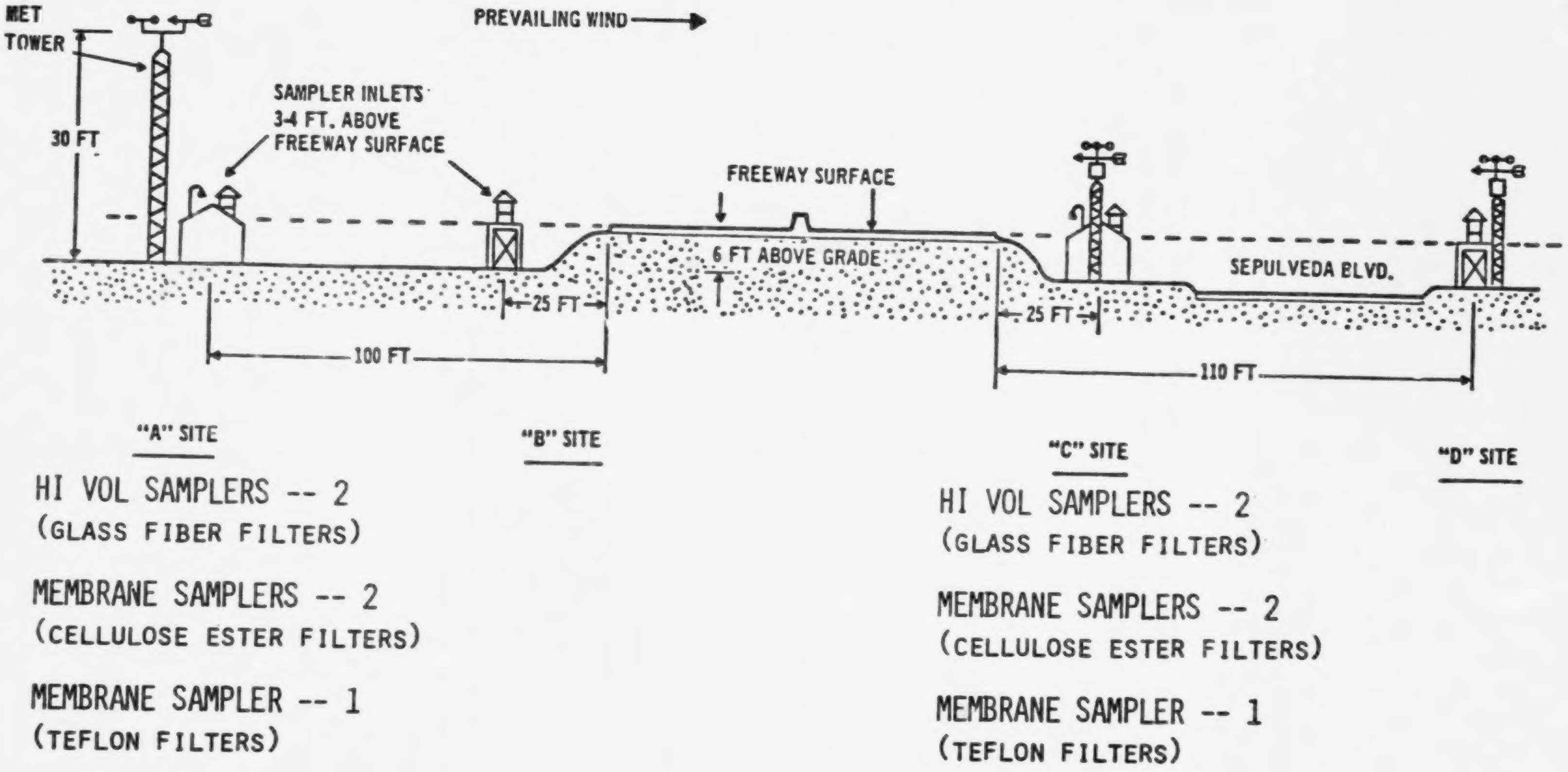
MET TOWER
30 FT
PREVAILING WIND
SAMPLER INLETS 3-4 FT. ABOVE FREEWAY SURFACE
FREEWAY SURFACE
6 FT ABOVE GRADE
SEPULVEDA BLVD.
25 FT
100 FT
25 FT
110 FT
"A" SITE
"B" SITE
"C" SITE
"D" SITE
HI VOL SAMPLERS -- 2
(GLASS FIBER FILTERS)
MEMBRANE SAMPLERS -- 2
(CELLULOSE ESTER FILTERS)
MEMBRANE SAMPLER -- 1
(TEFLON FILTERS)
HI VOL SAMPLERS -- 2
(GLASS FIBER FILTERS)
MEMBRANE SAMPLERS -- 2
(CELLULOSE ESTER FILTERS)
MEMBRANE SAMPLER -- 1
(TEFLON FILTERS)

Figure 4. Sample collection.

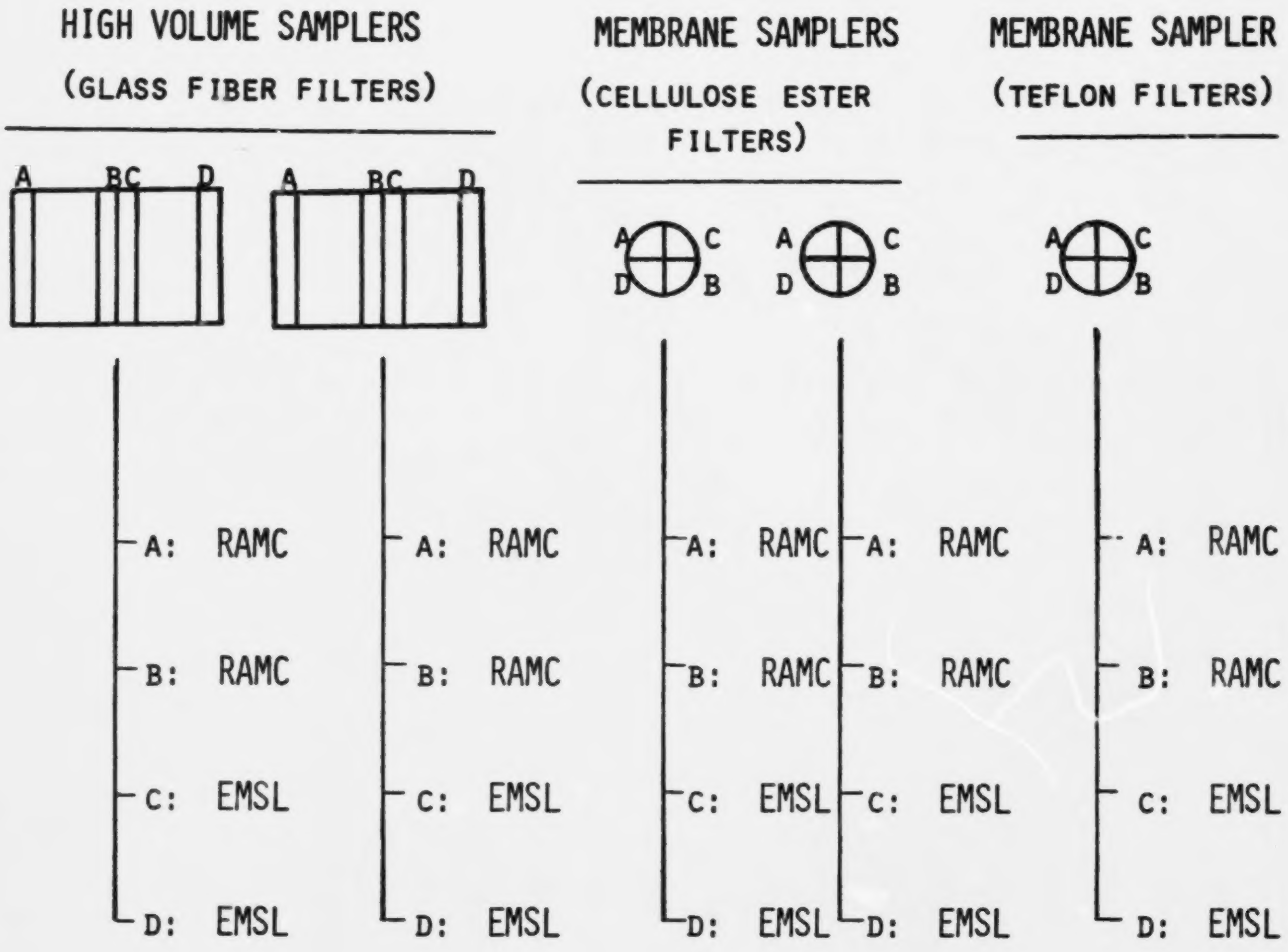
HIGH VOLUME SAMPLERS
(GLASS FIBER FILTERS)
MEMBRANE SAMPLERS
(CELLULOSE ESTER FILTERS)
MEMBRANE SAMPLER
(TEFLON FILTERS)
A
BC
D
A
BC
D
A
C
D
B
A
C
D
B
A
C
D
B
A: RAMC
B: RAMC
C: EMSL
D: EMSL
A: RAMC
B: RAMC
C: EMSL
D: EMSL
A: RAMC
B: RAMC
C: EMSL
D: EMSL
A: RAMC
B: RAMC
C: EMSL
D: EMSL
A: RAMC
B: RAMC
C: EMSL
D: EMSL

Figure 5. Sample analysis.

TABLE XIII. HI-VOL AT SITE A FOR TSP ($\mu g/m^3$)

Date	Sampler 1	Sampler 2
8/26/76	80.0	90.6
8/27/76	125.9	104.4
8/28/76	74.6	85.4
8/29/76	74.6	82.7
8/30/76	105.3	111.5
8/31/76	114.7	119.1
9/ 1/76	100.1	99.7
9/ 4/76	66.2	76.5
9/ 5/76	46.3	46.4
9/ 6/76	29.2	31.2
9/ 7/76	85.7	84.9
9/ 8/76	117.0	121.9
Average	85.0	87.9
Paired-t	-1.14	
Corr. Coeff.	0.95	

TABLE XIV. HI-VOL AT SITE C FOR TSP ($\mu g/m^3$)

Date	Sampler 1		Sampler 2
8/26/76	127.0		126.9
8/27/76	160.0		156.7
8/28/76	153.8		130.3
8/29/76	116.7		121.7
8/30/76	140.1		141.5
8/31/76	141.6		144.3
9/ 1/76	128.9		131.9
9/ 4/76	124.4		116.3
9/ 5/76	92.9		104.2
9/ 6/76	93.6		90.9
9/ 7/76	135.8		138.8
9/ 8/76	165.5		161.0
Average	131.7		130.4
Paired-t		+0.53	
Corr. Coeff.		0.93	

TABLE XV. MEMBRANE (CELLULOSE ESTER) AT SITE A FOR TSP ($\mu g/m^3$)

Date	Sampler 1		Sampler 2
8/26/76	75.8		53.9
8/27/76	137.5		129.5
8/28/76	85.6		70.8
8/29/76	104.8		93.6
8/30/76	133.9		102.0
8/31/76	100.2		101.1
9/ 1/76	75.6		91.3
9/ 4/76	95.9		73.9
9/ 5/76	111.0		101.0
9/ 6/76	85.5		64.9
9/ 7/76	131.2		156.5
9/ 8/76	208.1		214.2
Average	112.1		104.4
Paired-t		+1.58	
Corr. Coeff.		0.93	

TABLE XVI. MEMBRANE (CELLULOSE ESTER) AT SITE C FOR TSP (μg/m^3)

Date	Sampler 1	Sampler 2
8/26/76	179.8	111.7
8/27/76	194.3	179.2
8/28/76	138.1	229.8
8/29/76	134.3	134.6
8/30/76	174.5	155.5
8/31/76	159.6	150.2
9/ 1/76	159.1	141.7
9/ 4/76	103.1	128.5
9/ 5/76	114.3	140.2
9/ 6/76	179.1	185.4
9/ 7/76	216.6	255.0
9/ 8/76	270.5	284.3
Average	168.6	174.7
Paired-t	-0.54	
Corr. Coeff.	0.71	

TABLE XVII. MEMBRANE (TEFLON) AT SITE A FOR TSP (µg/m^3)

Date	Result
8/26/76	19.8
8/27/76	43.7
8/28/76	43.8
8/29/76	47.2
8/30/76	354.8*
8/31/76	81.9
9/ 1/76	76.0
9/ 4/76	39.1
9/ 5/76	33.8
9/ 6/76	20.3
9/ 7/76	60.9
9/ 8/76	86.3
Average	50.3

*Omitted from average

TABLE XVIII. MEMBRANE (TEFLON) AT SITE C FOR TSP (μg/m^3)

Date	Result
8/26/76	84.2
8/27/76	143.7
8/28/76	74.0
8/29/76	57.0
8/30/76	98.9
8/31/76	102.2
9/ 1/76	101.6
9/ 4/76	46.6
9/ 5/76	66.4
9/ 6/76	88.3
9/ 7/76	66.2
9/ 8/76	129.5
Average	88.2

TABLE XIX. HI-VOL AT SITE A FOR SO_4 ($\mu g/m^3$)

	Sampler 1				Sampler 2			
	RAMC		EMSL		RAMC		EMSL	
Date	Str. a	Str. b	Str. c	Str. d	Str. a	Str. b	Str. c	Str.d
8/26/76	16.1	16.5	15.7	16.1	16.2	17.0	16.9	16.8
8/27/76	39.3	42.7	41.9	41.9	40.9	43.0	45.8	44.5
8/28/76	23.4	23.0	24.1	22.8	23.9	22.8	24.2	24.8
8/29/76	14.1	14.2	14.7	14.4	14.8	14.9	15.6	15.5
8/30/76	13.5	14.0	14.1	13.2	14.0	13.6	14.2	13.7
8/31/76	15.4	15.5	14.6	16.1	15.1	15.9	16.1	17.0
9/ 1/76	23.2	23.9	24.5	22.7	25.3	25.0	25.2	25.4
9/ 4/76	11.5	11.2	11.2	10.6	12.3	11.8	12.4	12.1
9/ 5/76	10.3	10.7	10.2	10.4	9.5	10.7	10.6	10.9
9/ 6/76	6.8	7.5	7.5	7.7	7.8	7.9	7.9	7.6
9/ 7/76	8.0	8.3	8.1	8.3	8.5	8.1	8.7	8.0
9/ 8/76	11.6	12.3	12.0	12.5	12.7	12.3	12.5	12.8
Average	16.1	16.7	16.6	16.4	16.8	16.9	17.5	17.4

OVERALL SAMPLER AVERAGES: #1 = 16.4; #2 = 17.2

OVERALL LAB AVERAGES : RAMC = 16.6; EMSL = 17.0

OVERALL STRIP AVERAGES : End = 16.7; Center = 16.9

TABLE XX. HI-VOL AT SITE C FOR SO_4 ($\mu g/m^3$)

	Sampler 1				Sampler 2			
	RAMC		EMSL		RAMC		EMSL	
Date	Str. a	Str. b	Str. c	Str. d	Str. a	Str. b	Str. c	Str. d
8/26/76	16.5	16.0	16.1	16.7	15.2	15.0	15.7	15.4
8/27/76	37.4	38.3	40.4	39.1	36.8	36.6	40.5	38.1
8/28/76	19.8	20.0	21.5	21.6	19.7	19.1	15.9	22.0
8/29/76	13.9	13.9	13.9	13.9	13.5	13.3	15.8	15.8
8/30/76	14.3	14.0	13.0	13.5	14.4	13.7	15.9	16.2
8/31/76	14.5	14.4	14.0	13.6	14.7	14.4	15.2	14.6
9/ 1/76	22.1	22.9	22.9	21.0	21.7	21.4	22.4	24.1
9/ 4/76	12.4	11.8	13.4	12.4	11.7	11.7	11.4	11.0
9/ 5/76	13.5	13.4	13.4	16.3	12.6	12.4	12.6	12.0
9/ 6/76	11.8	11.3	11.7	11.8	10.6	11.0	10.7	10.7
9/ 7/76	14.0	13.3	13.5	13.5	12.3	14.3	12.8	12.6
9/ 8/76	14.1	14.4	13.6	13.9	13.8	13.9	12.3	12.6
Average	17.0	17.0	17.3	17.3	16.4	16.4	16.8	17.1

OVERALL SAMPLER AVERAGES: #1 = 17.2; #2 = 16.7

OVERALL LAB AVERAGES : RAMC = 16.7; EMSL = 17.2

OVERALL STRIP AVERAGES : End = 17.0; Center = 16.9

TABLE XXI. MEMBRANE (CELLULOSE ESTER) AT SITE A FOR SO_4 ($\mu g/m^3$)

	Sampler 1				Sampler 2			
	RAMC		EMSL		RAMC		EMSL	
Date	Qtr. a	Qtr. b	Qtr. c	Qtr. d	Qtr. a	Qtr. b	Qtr. c	Qtr. d
8/26/76	13.0	12.9	11.8	11.8	13.1	13.5	10.7	11.4
8/27/76	38.5	38.9	34.[illegible]	38.2	35.5	45.9	39.5	38.1
8/28/76	20.0	20.1	16.2	17.1	20.3	19.7	22.2	17.1
8/29/76	11.9	12.1	10.1	10.7	13.6	12.9	11.3	14.3
8/30/76	12.5	12.3	10.7	10.7	12.7	13.2	9.7	10.5
8/31/76	11.6	11.5	8.8	9.9	11.6	11.3	9.0	10.8
9/ 1/76	18.8	19.3	16.5	16.5	20.3	20.0	16.7	18.2
9/ 4/76	10.1	9.8	7.7	8.0	9.3	9.0	8.0	7.0
9/ 5/76	7.6	7.5	6.7	7.0	8.8	8.3	6.3	6.3
9/ 6/76	6.7	7.3	5.2	5.5	8.0	7.2	5.1	5.1
9/ 7/76	6.8	6.7	5.7	4.6	7.0	7.4	4.8	5.5
9/ 8/76	10.5	11.2	8.8	8.8	10.4	11.6	8.8	8.8

OVERALL SAMPLER AVERAGES: #1 = 13.1; #2 = 13.7

OVERALL LAB AVERAGES : RAMC = 14.3; EMSL = 12.5

TABLE XXII. MEMBRANE (CELLULOSE ESTER) AT SITE C FOR SO_4 ($\mu g/m^3$)

	Sampler 1				Sampler 2			
	RAMC		EMSL		RAMC		EMSL	
Date	Qtr. a	Qtr. b	Qtr. c	Qtr. d	Qtr. a	Qtr. b	Qtr. c	Qtr. d
8/26/76	14.7	14.0	9.4	10.1	14.4	13.0	10.8	12.34[a]
8/27/76	40.1	40.1	33.4	34.1	42.8	37.8	34.5	35.4
8/28/76	21.5	20.8	15.9	14.8	22.2	20.0	16.5	17.2
8/29/76	14.2	12.7	10.4	8.5	12.3	13.3	10.1	12.3
8/30/76	13.6	12.0	9.4	9.8	12.3	13.0	9.1	10.9
8/31/76	11.7	12.7	8.6	8.6	13.1	13.1	9.9	10.3
9/ 1/76	21.4	20.3	11.5	16.6	21.3	20.4	17.7	18.5
9/ 4/76	9.4	10.2	5.1	5.5	9.4	10.1	7.0	7.7
9/ 5/76	8.2	8.1	5.3	6.3	8.5	8.7	7.1	6.4
9/ 6/76	7.5	6.7	4.6	4.2	7.0	6.8	6.1	4.8
9/ 7/76	7.9	7.9	3.8	3.8	6.9	6.9	4.9	4.9
9/ 8/76	11.5	12.9	8.4	7.4	11.1	10.1	9.2	7.9

a: estimated

OVERALL SAMPLER AVERAGES: #1 = 12.8; #2 = 13.5

OVERALL LAB AVERAGES : RAMC = 14.9; EMSL = 11.4

TABLE XXIII. MEMBRANE (TEFLON) AT SITE A FOR SO_4 ($\mu g/m^3$)

	RAMC		EMSL	
Date	Qtr. a	Qtr. b	Qtr. c	Qtr. d
8/26/76	10.3	10.1	10.0	5.4
8/27/76	34.0	33.2	20.2	23.8
8/28/76	15.8	18.1	12.8	12.8
8/29/76	9.7	10.0	7.2	6.0
8/30/76	9.9	9.1	8.1	8.3
8/31/76	9.1	8.3	6.5	7.8
9/ 1/76	16.7	18.0	12.3	14.4
9/ 4/76	6.6	7.6	5.4	5.8
9/ 5/76	6.5	2.9	2.1	4.6
9/ 6/76	0.4	2.1	3.3	2.3
9/ 7/76	3.8	4.4	3.3	3.3
9/ 8/76	9.4	8.4	6.2	7.1

OVERALL LAB AVERAGES: RAMC = 11.0; EMSL = 8.3

TABLE XXIV. MEMBRANE (TEFLON) AT SITE C FOR SO_4 ($\mu g/m^3$)

	RAMC		EMSL	
Date	Qtr. a	Qtr. b	Qtr. c	Qtr. d
8/26/76	10.9	10.5	6.7	4.9
8/27/76	34.0	31.2	22.1	5.9
8/28/76	14.4	17.1	13.9	10.3
8/29/76	7.7	7.0	5.6	6.3
8/30/76	14.4	14.8	16.1	11.9
8/31/76	8.6	9.4	8.3	7.1
9/ 1/76	17.2	17.2	14.6	13.7
9/ 4/76	5.9	5.3	5.0	1.9
9/ 5/76	3.8	4.0	2.7	2.1
9/ 6/76	4.7	4.5	2.6	1.7
9/ 7/76	5.2	4.8	1.2	1.9
9/ 8/76	9.6	10.5	5.8	6.5

OVERALL LAB AVERAGES: RAMC = 11.4; EMSL = 7.5

TABLE XXV. SO_4 RANDOM MODELS

Data Sets:

		Site A	Site C
Method	HV	I	II
	M(c)	III	IV

Model: $$Y_{ijkl} = \mu + D_i + S_j + L_k + (DS)_{ij} + (DL)_{ik} + (SL)_{jk} + (DSL)_{ijk} + W(DSL)_{l(ijk)}$$

where D:	Day Effect	$\sim N\,(o,\sigma_D^2)$	$i = 1,2,\ldots.,12$
S:	Sampler Effect	$\sim N\,(o,\sigma_S^2)$	$j = 1,2$
L:	Lab Effect	$\sim N\,(o,\sigma_L^2)$	$k = 1,2$
W (DSL):	Experimental Error	$\sim N\,(o,\sigma_W^2)$	$l = 1,2$

Expected Mean Squares:

Source	df	EMS
Day	11	$8\sigma_D^2 + 4\sigma_{DS}^2 + 4\sigma_{DL}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
Sampler	1	$48\sigma_S^2 + 4\sigma_{DS}^2 + 24\sigma_{SL}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
Lab	1	$48\sigma_L^2 + 4\sigma_{DL}^2 + 24\sigma_{SL}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
DS	11	$4\sigma_{DS}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
DL	11	$4\sigma_{DL}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
SL	1	$24\sigma_{SL}^2 + 2\sigma_{DSL}^2 + \sigma_W^2$
DSL	11	$2\sigma_{DSL}^2 + \sigma_W^2$
W(DSL)	48	σ_W^2
	95	

Since membrane teflon filters (M(t)) are not routinely employed in the LACS and were not duplicated at each site, only the hi-vol (HV) and membrane cellulose ester (M(c)) results are considered for the estimation of variance components. The random effects model used to fit each data subset is shown in Table XXV, along with the resultant table of expected mean squares required for the estimation of variance components.

The results of analysis of variance are shown in Table XXVI for each of the four data subsets. The two- and three-factor interactions are tested in each case using the within mean square error (W(DSL)). Although the sampler by laboratory interaction is significant at the 95% level for the hi-vol data at site A, no interactions were significant at site C and the "pooled" (including interactions) mean square error at site C exceeds that at site A. Hence, it is probably reasonable to ignore interactions in further analysis. Similarly, the membrane data at site C indicate some interactions, but since none were evidenced at site A which has the larger pooled mean square error, no further account of interactions was taken.

Using the pooled mean square error, tests were made for the significance of the factors, sampler and laboratory in each data subset as shown by the bracketted F-statistics in Table XXVI. In each case, sampler and laboratory appear to exert a real influence on reported $SO_4^=$ *concentrations.*

VARIANCE COMPONENTS

Estimates of the variance components associated with $SO_4^=$ *measurements for each of the four method-site classifications appear in Table XXVII. By summing the estimates for the between sampler, between laboratory and within laboratory components in each case, an estimate of the overall variance associated with a reported* $SO_4^=$ *concentration is obtained as shown in the right hand column of the table.*

Comparing estimates of variance components of the same type between sites reveals differences as large as a factor of three. It should be noted, however, that the factors, sampler and laboratory are estimated with a single degree of freedom since only two of each were used to generate each data subset. Hence, if the variance ratios were tested by the F-statistic, the variance components for sampler and laboratory between sites (within method) would not be statistically different. These results, therefore, are pooled for each method and the result is shown as a coefficient of variation for comparison purposes. The within laboratory variance components, however, are estimated with 82 degrees of freedom each and the estimate for the hi-vol data at site C is statistically different than the corresponding estimate for site A with the variance at site C exceeding that at site A by a factor of two.

Estimates of the overall variance in TSP concentration for each data subset are shown in Table XXVIII. Again, the separate estimates by site were pooled and expressed as a coefficient of variation although the membrane results at site C showed considerably more variability than those at site A.

In Figure 6, the 4-hour variance components appear in bar graph format, expressed as coefficients of variation for comparison purposes.

TABLE XXVI. SO_4 ANOVA (RANDOM MODELS)

I. HV-Site A (overall mean = 16.79 $\mu g/m^3$)

Source	df	SS	MS	F
Day	11	8197.40	745.22	
Sampler	1	12.69	12.69	(27.00)**
Lab	1	3.19	3.19	(6.78)*
DS	11	8.33	0.76	2.77
DL	11	7.58	0.69	2.52
SL	1	1.73	1.73	6.35*
DSL	11	3.01	0.27	0.73
W(DSL)	48	18.07	0.38	
	95	8251.99	86.86	
(Pooled Error)	(82)	(38.71)	(0.47)	

II. HV-Site C (overall mean = 16.90 $\mu g/m^3$)

Source	df	SS	MS	F
Day	11	4924.15	447.65	
Sampler	1	5.32	5.32	(5.12)*
Lab	1	3.84	3.84	(3.69)*
DS	11	20.23	1.84	1.35
DL	11	14.23	1.29	0.95
SL	1	0.35	0.35	0.26
DSL	11	14.94	1.36	1.84
W(DSL)	48	35.52	0.74	
	95	5018.58	52.83	
(Pooled Error)	(82)	(85.27)	(1.04)	

NOTE: *indicates F is significant at P = 0.95
**indicates F is significant at P = 0.99

continued

TABLE XXVI. CONTINUED

III. M(c) - Site A (overall mean = 13.39 μg/m^3)

Source	df	SS	MS	F
Day	11	7092.97	644.82	
Sampler	1	7.54	7.54	(5.22)*
Lab	1	85.69	85.69	(59.28)**
DS	11	16.88	1.53	1.89
DL	11	3.99	0.36	0.45
SL	1	0.01	0.01	0.01
DSL	11	8.93	0.81	0.44
W(DSL)	48	88.71	1.85	
	95	7304.72	76.89	
(Pooled Error)	(82)	(118.52)	(1.45)	

IV. M(c) - Site C (overall mean = 13.14 μg/m^3)

Source	df	SS	MS	F
Day	11	6612.94	601.18	
Sampler	1	9.63	9.63	(7.12)**
Lab	1	292.60	292.60	(216.46)**
DS	11	8.58	0.78	1.44
DL	11	29.30	2.66	4.93 **
SL	1	18.03	18.03	33.38 **
DSL	11	5.94	0.54	0.53
W(DSL)	48	49.00	1.02	
	95	7026.01	73.96	
(Pooled Error)	(82)	(110.84)	(1.35)	

NOTE: *indicates F is significant at P = 0.95
**indicates F is significant at P = 0.99

TABLE XXVII. SO_4 VARIANCE COMPONENTS ESTIMATES ($cv = \frac{\hat{\sigma}}{\bar{\bar{x}}} \cdot 100\%$)

	$\hat{\sigma}_S^2 = \frac{MSS - MSEp}{48}$	$\hat{\sigma}_L^2 = \frac{MSL - MSEp}{48}$	$\hat{\sigma}_W^2 = MSEp$	$\hat{\sigma}_Y^2 = \hat{\sigma}_S^2 + \hat{\sigma}_L^2 + \hat{\sigma}_W^2$
I. HV-Site A	0.25	0.06	0.47	0.78
II. HV-Site C	0.09	0.06	1.04	1.19
AVERAGE	0.17 (2.4 %)	0.06 (1.5 %)	0.76 (5.2 %)	0.99 (5.9 %)
III. M(c)-Site A	0.13	1.76	1.45	3.33
IV. M(c)-Site C	0.17	6.07	1.35	7.59
AVERAGE	0.15 (2.9 %)	3.91 (14.9 %)	1.40 (8.9 %)	5.46 (17.6 %)

Table XXVIII. TSP VARIANCE COMPONENT ESTIMATES $(cv = \frac{\hat{\sigma}}{\bar{x}} \cdot 100\%)$

	$\hat{\sigma}_S^2 = \frac{1}{12} \sum_{i=1}^{12} \frac{1}{2} (S_{1i} - S_{2i})^2$
I. HV - Site A	39.57
II. HV - Site C	34.84
AVERAGE	37.21 (5.6 %)
III. M(c) - Site A	159.94
IV. M(c) - Site C	710.31
AVERAGE	435.13 (14.9 %)

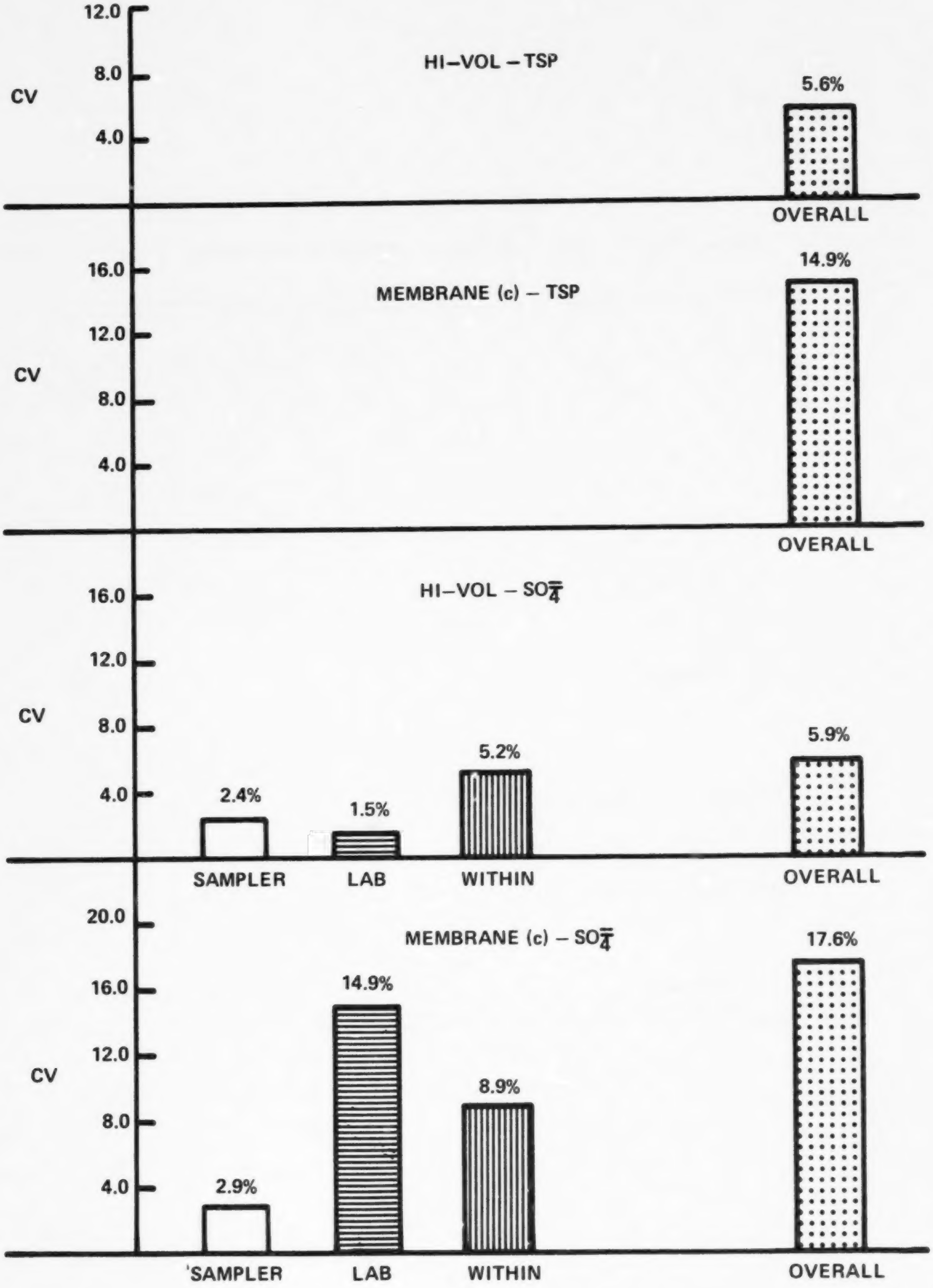

Figure 6. Four-hour variance components ($CV=\frac{\hat{\sigma}}{x} \cdot 100\%$).

SAMPLING SITE AND METHOD EFFECTS

The TSP data by sampling site, method and date (averaged over duplicate samplers) appear in Table XXIX. The fixed effects model shown in Table XXX was used to fit the data for the purpose of testing site and method effects. As shown in the analysis of variance, both site and method effects are apparently real for TSP results. Partitioning the two degrees of freedom for method reveals that while the membrane samplers produce significantly different results depending on filter material used (cellulose ester or teflon), the average membrane results did not differ significantly from the hi-vol results.

Table XXXI shows the $SO_4^=$ data by sampling site, method and date (averaged over duplicate filter partitions, laboratory and sampler). A similar fixed effects model was used to fit these data and the results appear in Table XXXII. In this case, the site effect was not significant, implying that there is no evidence in the data from this twelve day study to suspect a significant contribution of $SO_4^=$ from the freeway. The differences among methods were significant, however, whether viewed as differences between sampler types or between filter materials within membrane samplers.

The average TSP data are plotted by site and day of study in Figure 7. While the three methods seem to generally fluctuate together, a great deal of scatter remains. In general, the membrane teflon filters show the lowest TSP loadings at either site while the membrane cellulose ester filters show the highest. The cross-freeway differences are plotted at the top of the figure. Although there is still a great deal of between method variability, all differences are positive with an average freeway contribution of about 50 $\mu g/m^3$ for the study.

Figure 8 is a similar set of plots for the average $SO_4^=$ data. The between method correlation for $SO_4^=$ results is obviously very high (actually, $r>.99$ for any pair of methods at either site). Also, it is interesting to note that the order of methods is very consistent with the glass fiber filters showing the largest $SO_4^=$ concentration, followed by the cellulose ester filters and, finally, the teflon filters. The cross-freeway differences for $SO_4^=$ are generally small (note that the scale is expanded) and, as previously discussed, are not significantly different from zero for the twelve day study period.

CONCLUSIONS

The major conclusions which may be drawn from the 24-hour high volume sampler study are as follows:

(1) Sample collection is not a significant source of error.

(2) Laboratory is a significant source of error for all pollutants except $SO_4^=$.

(3) Variability among filter strips is the largest source of error for all pollutants.

(4) Variability among chemical analyses is relatively minor for all pollutants.

TABLE XXIX. AVERAGE TSP ($\mu g/m^3$)

	SITE A			SITE C		
Date	HV	M(c)	M(t)	HV	M(c)	M(t)
8/26/76	85.3	64.9	19.8	127.0	145.8	84.2
8/27/76	115.2	133.5	43.7	158.4	186.8	143.7
8/28/76	80.0	78.2	43.8	142.1	184.0	74.0
8/29/76	78.7	99.2	47.2	119.2	134.5	57.0
8/30/76	108.4	118.0	354.8	140.8	165.0	98.9
8/31/76	116.9	100.7	81.9	143.0	154.9	102.2
9/ 1/76	99.9	83.5	76.0	130.4	150.4	101.6
9/ 4/76	71.4	84.9	39.1	120.4	115.8	46.6
9/ 5/76	46.4	106.0	33.8	98.6	127.3	66.4
9/ 6/76	30.2	75.2	20.3	92.3	182.3	88.3
9/ 7/76	85.3	143.9	60.9	137.3	235.8	66.2
9/ 8/76	119.5	211.2	86.3	163.3	277.4	129.5
Overall Average	86.4	108.3	75.6	131.1	171.7	88.2

TABLE XXX. TSP FIXED MODEL

Data Set: Average TSP concentration by Date, Site and Method

Model: $Y_{ijk} = \mu + D_i + S_j + M_k + (DS)_{ij} + (DM)_{ik} + (SM)_{jk} + (DSM)_{ijk}$

where D: Day Effect (fixed) $i = 1,2,....,12$

S: Site Effect (fixed) $j = 1,2$

M: Method Effect (fixed) $k = 1,2,3$

ANOVA:

Source	df	SS	MS	F
Day	11	61,090.55	5,553.69	4.29**
Site	1	29,090.73	29,090.73	22.50**
Method	2	40,469.38	20,234.69	15.65**
HV vs. avg. M	1	78.18		0.06
M(c) vs. M(T)	1	40,391.20		31.24**
DS	11	20,464.84	1,860.44	1.44
DM	22	44,666.47	2,030.29	1.57
SM	2	7,922.78	3,961.39	3.06
DSM	22	28,447.95	1,293.09	
	71	232,152.70	3,269.76	

NOTE: * indicates F is significant at P = 0.95
** indicates F is significant at P = 0.99

TABLE XXXI. AVERAGE SO_4 ($\mu g/m^3$)

Date	SITE A HV	SITE A M(c)	SITE A M(t)	SITE C HV	SITE C M(c)	SITE C M(t)
8/26/76	16.41	12.28	8.95	15.83	12.34	8.25
8/27/76	42.50	38.68	27.80	38.40	37.28	23.30
8/28/76	23.63	19.09	14.88	19.95	18.61	13.93
8/29/76	14.78	12.18	8.23	14.25	11.73	6.65
8/30/76	13.79	11.54	8.85	14.38	11.26	14.30
8/31/76	15.71	10.56	7.93	14.43	11.00	8.35
9/ 1/76	24.40	18.29	15.35	22.31	18.46	15.68
9/ 4/76	11.64	8.61	6.35	11.98	8.05	4.53
9/ 5/76	10.14	7.31	4.03	13.28	7.33	3.15
9/ 6/76	7.59	6.26	2.03	11.20	5.96	3.38
9/ 7/76	8.25	6.06	3.70	13.29	5.88	3.28
9/ 8/76	12.34	9.86	7.78	13.58	9.81	8.10
Overall Average	16.79	13.39	9.66	16.91	13.14	9.41

TABLE XXXII. SO_4 FIXED MODEL

Data Set: Average SO_4 concentration by Date, Site and Method

Model: $Y_{ijk} = \mu + D_i + S_j + M_k + (DS)_{ij} + (DM)_{ik} + (SM)_{jk} + (DSM)_{ijk}$

where D: Day Effect (fixed) $i = 1,2,....,12$

S: Site Effect (fixed) $j = 1,2$

M: Method Effect (fixed) $k = 1,2,3$

ANOVA:

Source	df	SS	MS	F
Day	11	4108.79	375.53	222.34**
Site	1	0.29	0.29	0.17
Method	2	642.23	321.11	191.14**
HV vs. Avg. M	1	474.65		282.53**
M(c) vs. M(t)	1	169.58		99.75**
DS	11	36.66	3.33	1.98
DM	22	131.29	5.97	3.55**
SM	2	0.54	0.27	0.16
DSM	22	37.01	1.68	
	71	4956.82	69.81	

NOTE: *indicates F is significant at $P = 0.95$
**indicates F is significant at $P = 0.99$

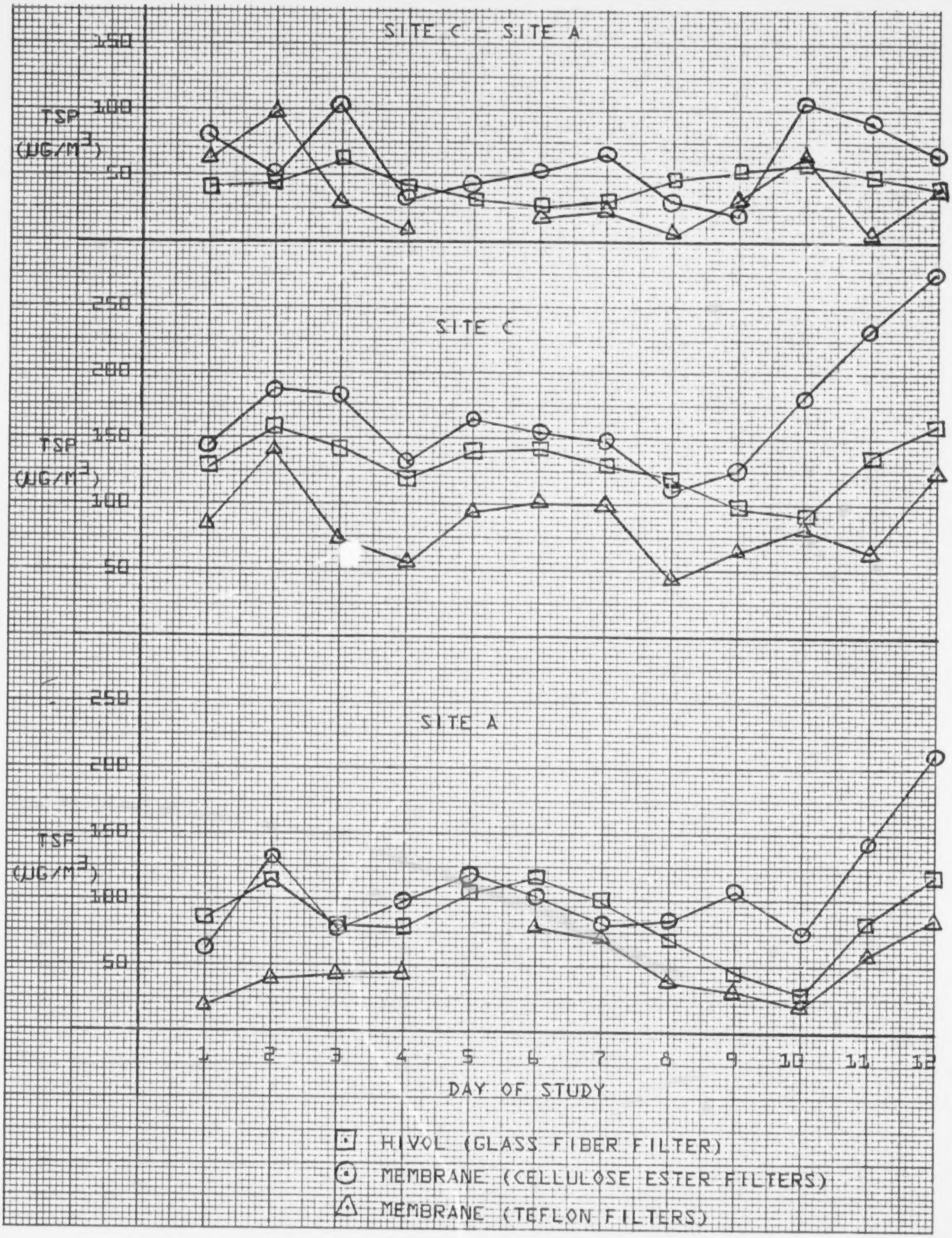

Figure 7. TSP concentrations.

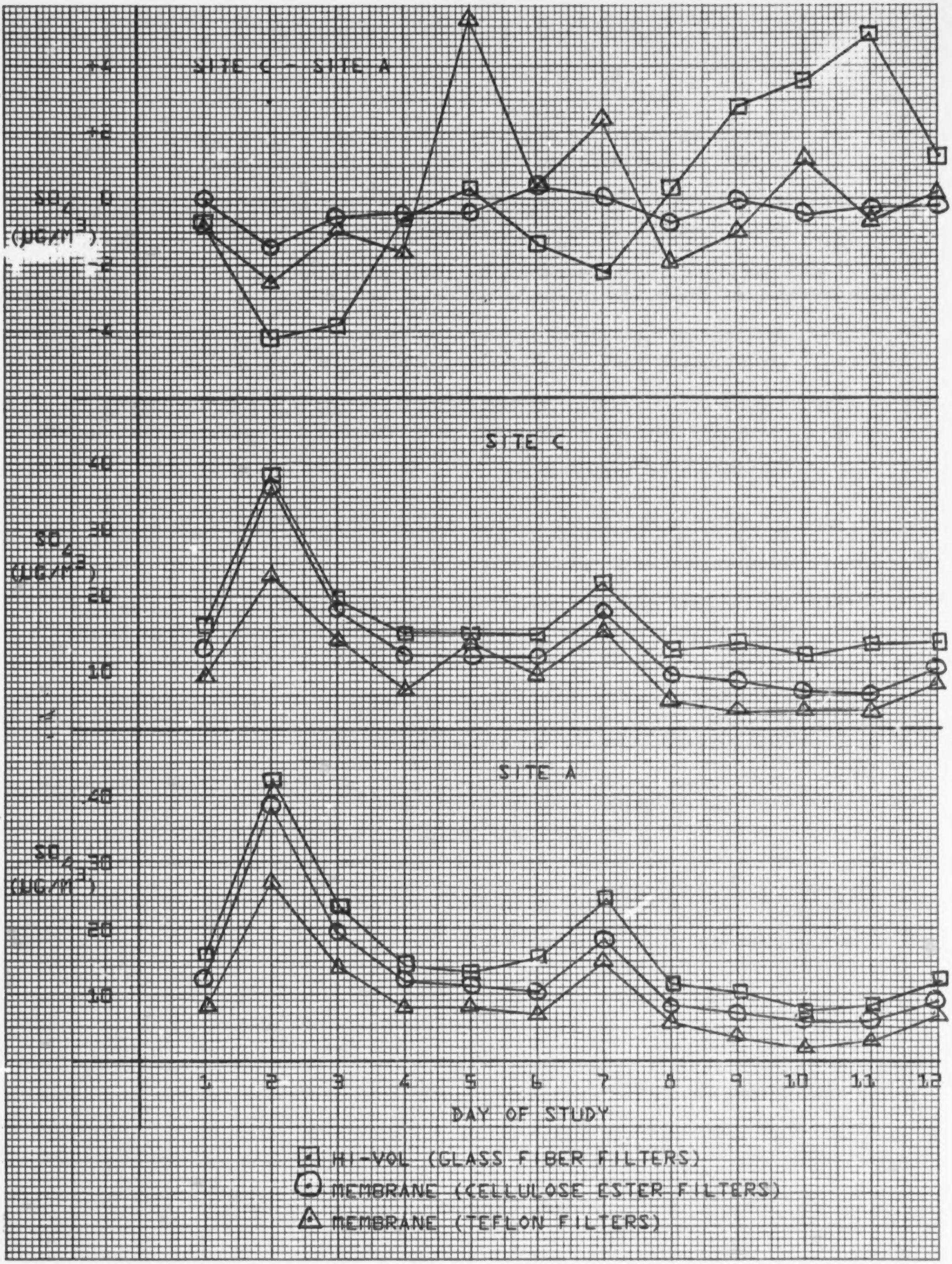

Figure 8. Sulfate concentrations.

(5) Strips cut from the center of filters tend to be slightly (<5%) higher in concentration than those cut from the ends.

(6) The time lag between sample collection and chemical analysis is a serious source of error in the determination of NH_4^+.

The major conclusions which may be drawn from the 4-hour high volume and membrane sampler study are as follows:

(1) The overall TSP precision for 4-hour hi-vol samples is only slightly greater than that for 24-hour samples (5.6% versus 5.2%).

(2) Though sample collection and laboratory are significant sources of error for $SO_4^=$ determination from 4-hour hi-vol samples, the overall $SO_4^=$ precision is only slightly greater than that for 24-hour samples (5.9% versus 3.9%).

(3) The overall TSP precision for 4-hour membrane samples (cellulose ester filters) is approximately three times that for 4-hour hi-vol samples (14.9% versus 5.6%).

(4) The overall $SO_4^=$ precision for 4-hour membrane samples (cellulose ester filters) is approximately three times that for 4-hour hi-vol samples (17.6% versus 5.9%).

(5) TSP concentrations appear to be dependent upon filter material employed (i.e., cellulose ester or teflon), though not necessarily upon sampler type (i.e., hi-vol or membrane).

(6) $SO_4^=$ concentrations are very dependent upon filter material employed with the following ranking in the order of descending concentration: hi-vol glass fiber, membrane cellulose ester, membrane teflon.

COMPARISON OF THE DEGRADATION OF AMMONIUM ION ON HIGH VOLUME GLASS FIBER FILTERS AND ON MEMBRANE FILTERS

George Colovos
Edward P. Parry

Rockwell International
Newbury Park, California

and

Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

The results of a study on the degradation of particulate ammonium ion collected on various filtering media are presented. The mechanism for the loss of ammonia from glass fiber filters is given. This mechanism is based on two assumptions: (1) that the residual alkalinity of the glass fibers is responsible for the loss of ammonium and; (2) that the rate of this loss is determined by the diffusion of this residual alkalinity from within the fiber to the surface. The effect of storage on the analysis of ammonium ion particulate collected on cellulose ester filters and Teflon filters is also discussed.

INTRODUCTION

Undesirable artifacts associated with the analysis of particulates collected on glass fiber filters have been reported for species such as sulfate ion ($SO_4^=$) and nitrate ion (NO_3^-). Several studies are currently underway to examime the phenomena connected with the transformation of sulfur dioxide ($SO_2^=$) to $SO_4^=$ and nitrogen dioxide/nitrogen oxide (NO_2/NO) to NO_3^- on the filter.

The degradation of particulate ammonium ion (NH_4^+) collected on such filter media came to attention through the external quality control (split sample program) applied to the analysis of the high-volume samples of the Los Angeles Catalyst Study (LACS). The wide disagreement between the two laboratories (Rockwell-Air Monitoring Center and Environmental Monitoring and Support Laboratory/Environmental Protection Agency) participating in the analysis of ammonium split samples suggested the possibility of loss of ammonium from the filters during storage. This hypothesis was also supported by the known high alkalinity of the glass fiber material, which can cause such a loss of ammonia from the samples. To test this hypothesis, old LACS particulate samples collected on glass fiber filters previously analyzed for ammonium were analyzed again. The second determination yielded consistently lower results, verifying the loss of particulate ammonium. At the same time, however, it was realized that these results were insufficient for explaining the mechanism of degradation of the ammonium species on glass fiber filter samples.

This paper presents the results of the study subsequently conducted to examine the loss of ammonium from particulates collected on glass fiber filters.

Additional experimental work for verifying the proposed mechanism of degradation of particulate ammonium from glass fiber filters is suggested in this paper. Some preliminary observations on the stability of particulate ammonium collected on cellulose ester and Fluoropore filters are also presented.

EXPERIMENTAL

High-volume samplers operating at the LACS sites were utilized to collect the particulate samples used in this study. The glass fiber filters that were used were specially made for the LACS study by Gelman, and were very similar to the Gelman type A/E filters. Three groups of three filters samples containing variable amounts of particulates were collected and analyzed in this study. Immediately after the collection, each group of samples was carried to the laboratory for processing. Upon arrival several 3/4" x 8" strips were cut from the exposed portion of each filter. These strips were used for the study of the kinetics of the degradation of the ammonium. The first strip from each filter was extracted immediately and the extract stored in the refrigerator for analysis. The other strips were folded in half with the exposed side in, placed in glassine envelopes and kept in the constant humidity and temperature weighing room (RH 40 ± 5% and 72° F) for subsequent analysis. Additional extractions of sample strips were performed on the 2nd, 3rd, 4th, 7th (or 8th), 21st, (or 22nd), 28th, and 35th (only for the third group) day after completion of sampling and stored again in the refrigerator for analysis. The extracts were analyzed with the next batch of regular LACS samples. The automated indophenol method was used for determining the ammonium concentration in the extracts.

The same procedures were used for the analysis of the membrane samples. In this case, each filter was divided into four quarters. The filter quarters were stored and analyzed the same way as the glass fiber samples.

RESULTS AND DISCUSSION

Tables I, II, and III give the results of the determination of particulate ammonium on high-volume glass fiber filters as a function of storage time. The analytical data are expressed in μg of NH_4^+ per ml of the extract (50 ml total). No effort was made to convert the data to other concentration units because, as will be shown, the degradation is a first order reaction (the rate constant of which is given in t^{-1}) and therefore arbitrarily chosen

TABLE I. DEGRADATION OF AMBIENT PARTICULATE AMMONIUM
ON GLASS FIBER FILTERS
SAMPLING PERIOD 165-166 JULIAN DATA
(GROUP I)

Extraction Date	Storage Time (Days)	NH_4^+ Concentration in μg/ml(*) Sample #1	 Sample #2	 Sample #3
166	0	15.9	14.4	12.5
167	1	15.3	14.2	12.0
168	2	14.1	13.8	12.0
169	3	14.4	13.9	11.5
170	4	12.9	13.5	11.3
173	7	12.7	11.2	10.8
173 DUP	7	12.7	11.4	10.0
180	14	12.3	8.9	9.6
188	22	10.6	9.2	9.0
194	28	10.0	8.4	6.8
	Estimated OH^- Concentration	6.0	6.2	4.4

(*) 1/12 of the sample extracted in 50 ml of aqueous acetate buffer.

TABLE II. DEGRADATION OF AMBIENT PARTICULATE AMMONIUM ON GLASS FIBER FILTERS

SAMPLING PERIOD 179-180 JULIAN DATE

(GROUP II)

Extraction Date	Storage Time (Days)	NH_4^+ Concentration in μg/ml(*) Sample #1	Sample #2	Sample #3
180(**)	0	7.7	10.1	8.8
180(***)	0	7.7	9.5	9.8
181	1	7.0	8.4	8.8
182	2	6.4	8.8	8.6
183	3	6.6	8.0	8.3
184	4	6.0	8.2	7.8
188	8	5.5	6.8	7.4
194	14	5.2	6.6	6.2
201	21	4.8	5.3	6.6
208	28	4.2	6.4	5.3
	Estimated OH^- Concentration	3.7	4.5	4.6

(*) 1/12 of the sample extracted in 50 ml of aqueous acetate buffer

(**) Strip from the end of the filter

(***) Strip from the middle of the filter

TABLE III. DEGRADATION OF AMBIENT PARTICULATE AMMONIUM ON GLASS FIBER FILTERS

SAMPLING PERIOD 172-173 JULIAN DATE

(GROUP III)

Extraction Date	Storage Time (Days)	NH_4^+ Concentrations in μg/ml(*) Sample #1	Sample #2	Sample #3
173(**)	0	5.6	5.3	4.8
173(***)	0	6.0	5.2	4.5
174	1	4.9	5.0	4.5
175	2	4.3	3.7	4.4
176	3	4.6	4.4	4.0
177	4	4.2	4.4	4.1
180	7	3.9	4.0	3.8
188	15	3.0	2.9	2.6
194	21	2.4	2.4	2.1
201	28	1.7	2.3	1.5
208	35	1.1	1.1	0.9
	Estimated OH^- Concentration	5.0	3.6	3.9

(*) 1/12 of the sample extracted in 50 ml of aqueous acetate buffer

(**) Strip from the end of the filter

(***) Strip from the middle of the filter concentration units can be used. The concentration of hydroxyl ion (OH^-) was estimated from the empirical rate curve. The following assumptions were made in this estimation: (1) the empirical rate curve should level off after reaction of all the available OH^-; and (2) the difference between the high (zero storage time) and the low points of the curve should be a measure of the amount of OH^- present in each filter. The low point of the curve was estimated by visual extrapolation of the empirically best fit curve. Due to the similar formal weights of the NH_4^+ and OH^- (18 and 17, respectively) and the relative imprecision of the curve extrapolation, no effort was made to convert the difference between high and low ammonium concentration to the equivalent OH^- concentration.

Figures 1 - 3 graphically present the data given in Table I - III. All of the curves in these figures are not the empirically best curves, but those based on the postulated mechanism of the ammonium degradation. It is evident that the agreement between the theoretical curve and the experimental result is rather close. These figures also show that the percentage of the total loss of ammonium ranges from about 35% for the most concentrated samples to about 82% for the less concentrated samples. However, as is shown in Table IV, the total loss of ammonium does not appear to depend on the initial ammonium concentration and, therefore, the loss should be attributed to reaction between NH_4^+ and some species present in the sample. If it is assumed that the reactive species is the OH^- of the glass fibers, then the following mechanism can be postulated:

$$OH^-_{(g)} \xrightarrow{slow} OH^-_{(s)} \qquad (1)$$

$$NH_4^+ \rightleftarrows NH_3 + H^+ \qquad (2)$$

and

$$OH^-_{(s)} + H^+ \longrightarrow H_2O \qquad (3)$$

or by combining (2) and (3)

$$NH_4^+ + OH^-_{(s)} \longrightarrow NH_3 \uparrow + H_2O \quad . \qquad (4)$$

According to this mechanism, the reaction shown in Equation (1) is the rate determining step and represents the diffusion of the OH^- from inside the glass fiber ($OH^-_{(g)}$) to the fiber-particulate interface ($OH^-_{(s)}$). Therefore, if this is the reaction mechanism, the rate expression should be given by Equation (5):

$$-\frac{d[OH]}{dt} = k[OH^-_{(g)}], \qquad (5)$$

where $[OH^-_{(g)}]$ is the concentration of OH^- inside the fiber at time t. Also,

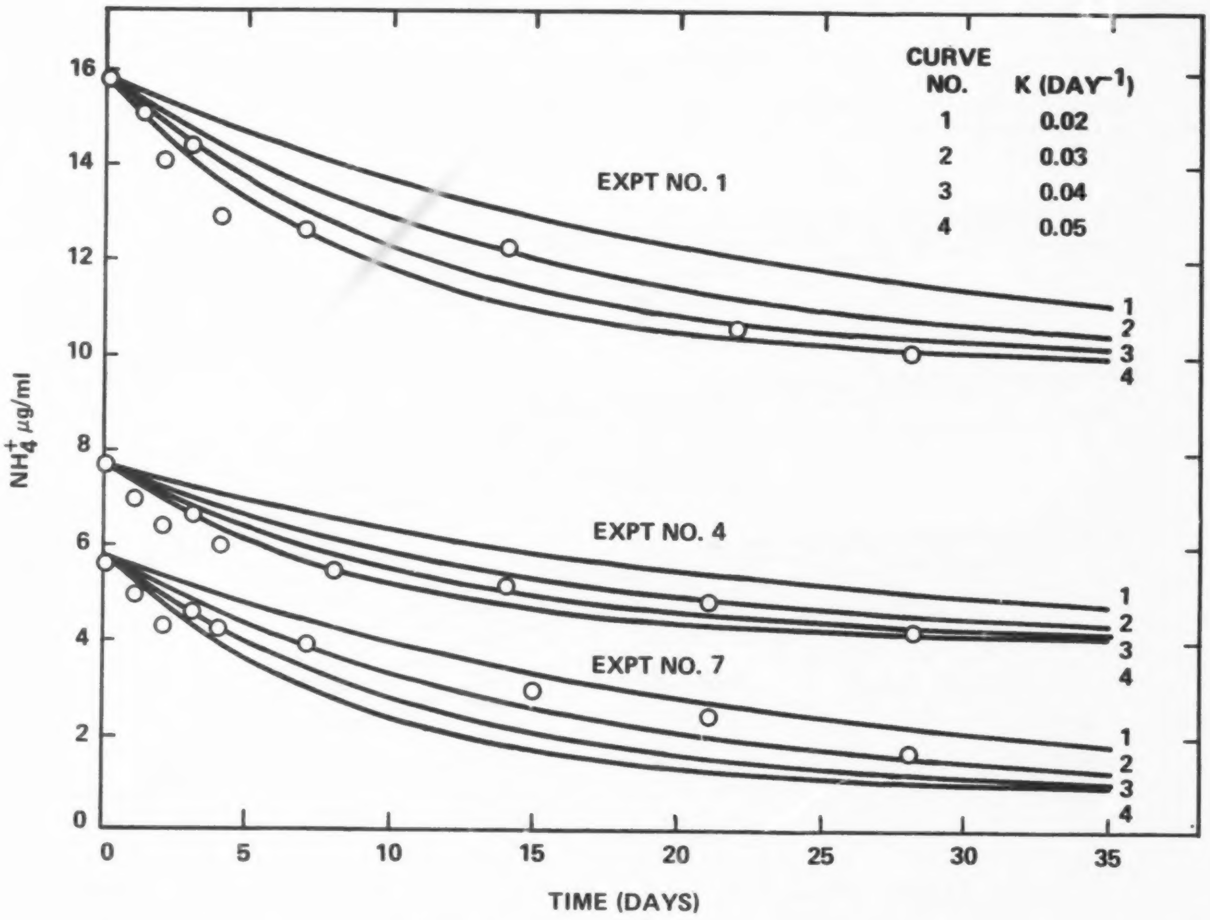

Figure 1. Changes of the NH_4^+ concentration in high-volume glass fiber filter samples with time.

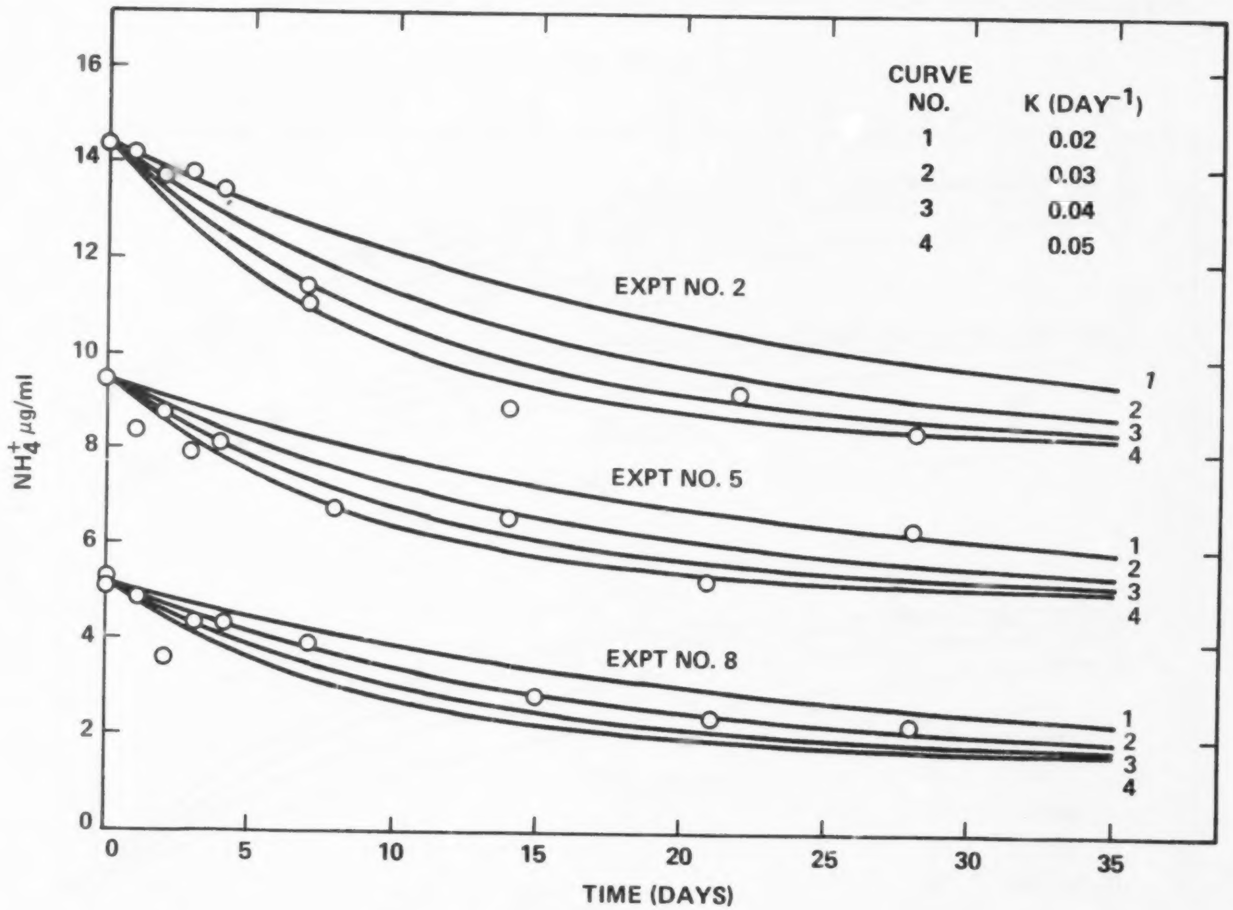

Figure 2. *Changes of the NH_4^+ concentration in high-volume glass fiber filter samples with time.*

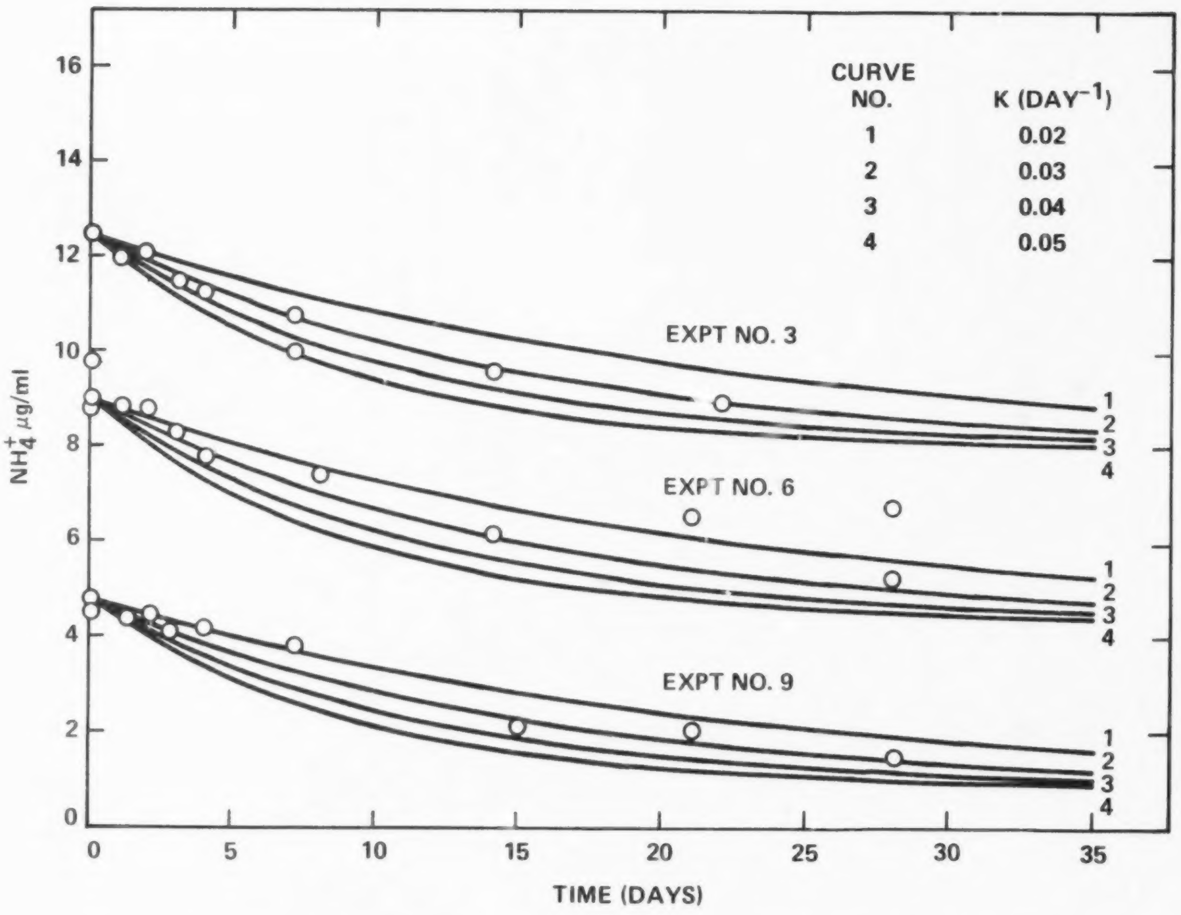

Figure 3. Changes of the NH$_4^+$ concentration in high-volume glass fiber filter samples with time.

TABLE IV. TOTAL LOSS OF AMMONIUM FROM THE SAMPLES

	NH_4^+ µg/ml	
Sample #	Initial Conc.	Total loss
1	15.9	6.0
2	14.4	6.2
3	12.5	4.4
4	7.7	3.7
5	10.1	4.5
6	8.8	4.6
7	5.6	5.0
8	5.3	3.6
9	4.8	3.9
	Average	4.66 ± 0.94 Std. Dev.

if the assumption is made that the surface OH^- reacts quickly with particulate NH_4^+ to produce gaseous ammonia (NH_3) which escapes from the sample immediately, then it can be easily proven that the concentration of OH^- inside the fibers will be given by Equation (6) below:

$$[OH^-_{(g)}] = C + [NH_4^+] \ ,$$

where C is the difference of the initial OH^- and NH_4^+ concentrations and $[NH_4^+]$ is the concentration of NH_4^+ at the time t. Obviously Equation (5) can now be modified to

$$\frac{d(C + [NH_4^+])}{(C + [NH_4^+])} = k \, dt \qquad (7)$$

or

$$\log (C + [NH_4^+]) = -kt + \text{const} \qquad (8)$$

or

$$t = \frac{1}{k} \log \frac{[OH^-_{(g)}]'}{C + [NH_4^+]} \ , \qquad (9)$$

where $[OH^-_{(g)}]'$ is the initial OH^- concentration in the fibers. Equation (9) gives the rate expression for the postulated mechanism of degradation of NH_4^+ on glass fiber filters. Figure 4 gives the plot of the average values of all the experimental points versus time according to Equation (9), and Table V gives the rate constants estimated from the individual experiments. The individually determined rate constants were calculated by eliminating values which obviously were outlying the rate expression. From the nine experiments, the experimental points of only one or perhaps two appear to fit the proposed rate expression very satisfactorily. In the rest of the runs, some points at random appear to deviate significantly from the rate expressing curve but the rest of them fit the rate expression satisfactorily. Also, if a rate constant close to the one obtained by averaging all the experimental points or that obtained by averaging the individually calculated rate constants is used for the reconstruction of each experimental run, the agreement between the experimental results and the postulated rate expression will be rather good.

Figures 1 - 3 present the experimental results in relation to the curves drawn by assuming four different rate constants ($k = 0.02$; $k = 0.03$, $k = 0.04$ and $k = 0.05$). Inspection of all the runs shows that a rate constant in the range of 0.035 - 0.045 day^{-1} may represent the ammonium degradation phenomena. The apparent scatter of the experimental data can be attributed to several factors which can be predicted to affect the results. Among them, temperature,

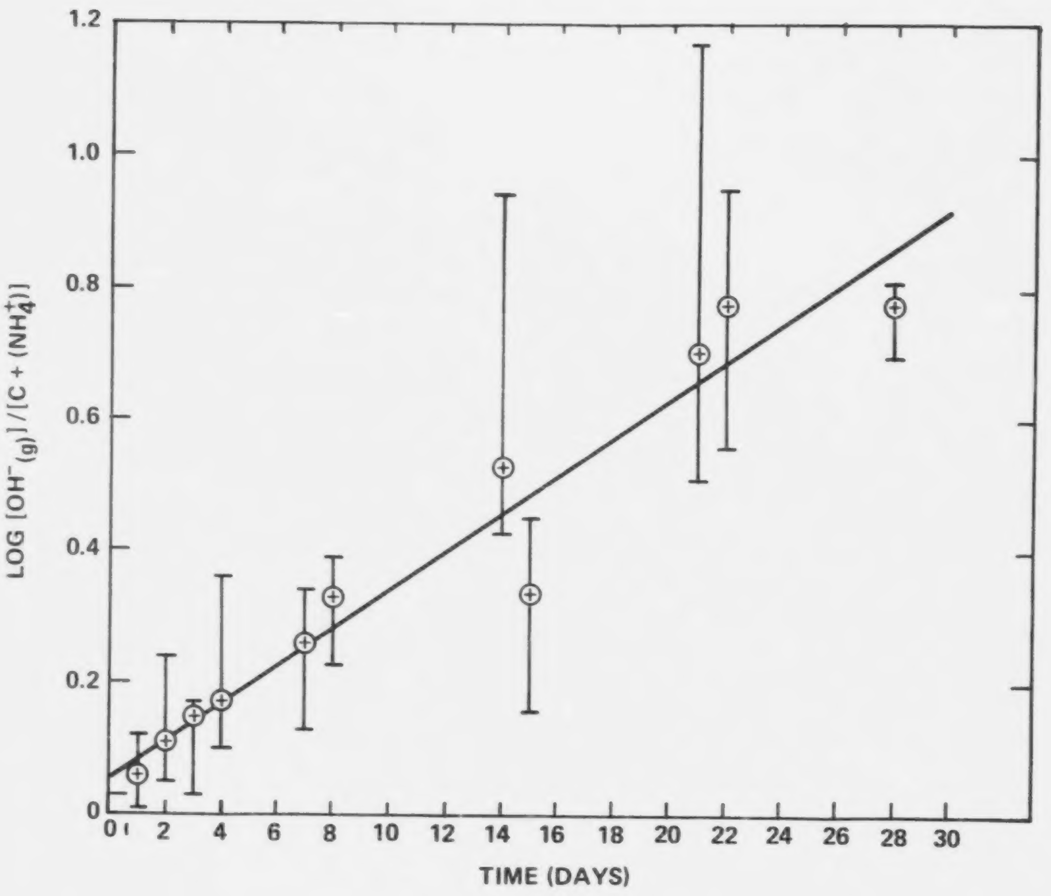

Figure 4. *Plot of the average experimental values of lo* $([OH^-_{(g)}]/(C + [NH_4^+]))$ *vs time.*

TABLE V. REACTION RATE CONSTANTS ESTIMATED FROM EQUATION (9)

Sample #	K (day^{-1})
1	0.053
2	0.051
3	0.044
4	0.038
5	0.027
6	0.023
7	0.024
8	0.026
9	0.028
	Average k 0.035 ± 0.011

humidity, barometric pressure, nature of glass fiber, alkalinity of fibers and last, but not least, the nature of the particulate and concentration of gaseous pollutants such as NH_3, SO_2, nitrogen dioxide (NO_2), etc. should be considered. In order to investigate the effect of these parameters on the ammonium degradation process, experiments under controlled conditions may be necessary. Controlled experimental conditions can be obtained by generating aerosol atmospheres containing NH_4^+ from which samples on glass fiber filters as well as on other filtering media can be generated. After collection, the filter samples should be stored in a controlled atmospheric chamber with adjustable humidity and temperature levels. Also, the alkalinity of the filters (OH^- concentration) should be determined independently. This can be done by determining the OH^- concentration in filter extracts by applying a Gran titration technique similar to the one currently used for determination of strong acid in airborne particulates. The same technique is also useful in measuring the total OH^- in the samples as a function of time. In fact, since the postulated mechanism is based on the hypothesis of the diffusion of OH^- in the fibers, determination of the total OH^- in the samples constitutes a direct test of this theory.

The results presented above clearly indicate that the degradation of particulate ammonium collected on glass fiber filters is an important artifact which may affect the data by as much as 89% or more, depending on the loading and the alkalinity of the filters. Theoretically, a factor based on the rate constant and the alkalinity of the filters can be applied to correct the data for degradation occurring during storage, but because of the relatively wide scatter of the results, this may not produce sufficiently accurate data. For example, if $k = 0.035\ day^{-1}$ and the initial concentration of OH^- is $[OH^-]'$, then the initial concentration of NH_4^+ will be given by Equation (10)

$$[NH_4^+]_{initial} = [OH^-]'(1-10^{-0.035t}) + [NH_4^+], \quad (10)$$

where $[NH_4^+]$ is the concentration of ammonium found on the filter after t days of storage. If Equation (10) is used for the data presented in Tables I, II, and III, the calculated initial concentrations agree rather well (within 10%) with those found when values obtained in the first week after sample collection are used. The correction of results corresponding to later analyses resulted in values considerably higher than the initial determination. Apparently the problem of degradation of particulate ammonium on glass fiber filters suggests that other filtering media may be more applicable for determining airbone ammonium. Preliminary results from a study currently underway have shown that cellulose ester and Teflon filters do not show significant loss of ammonium immediately after collection of the samples. Table VI demonstrates the effect of one week's storage on particulate ammonium collected on both Teflon and cellulose ester filters. The observed differences are rather small, indicating the compatibility of these filters with the analysis of particulate ammonium. Complete evaluation of these and other filtering media will be possible after the completion of the study presently underway.

TABLE VI. EFFECT OF STORAGE ON THE ANALYSIS OF PARTICULATE AMMONIUM COLLECTED ON CELLULOSE ESTER FILTERS

$\mu g/ml\ NH_4^+$ In the Extract

Teflon		Cellulose Ester	
Immediately After Collection	One Week After Collection	Immediately After Collection	One Week After Collection
0.82	0.73	3.46	2.56
0.96	0.72	4.27	4.92
2.90	2.72	3.32	2.51
0.67	0.93	2.61	2.45
		1.22	1.30

SULFATE CONCENTRATIONS AT TWO LOS ANGELES FREEWAYS

A.H. Bockian, George Tsou, Dennis Gibbons, and Robert Reynolds
California Air Resources Board
El Monte, California

ABSTRACT

The Air Resources Board has sampled for particulates during 1975 and 1976 at the San Diego freeway (and more briefly at the Hollywood freeway) in order to determine the increase in atmospheric sulfate caused by sulfate emissions from catalyst equipped vehicles. Twelve 2-hour samples were obtained daily, three days per week, at upwind and downwind sites at each location. An automotive sulfate contribution is evident at each freeway. The maximum contribution seems to occur at midday when traffic counts are high, traffic is moving rapidly, and a moderate wind is blowing across the freeway. Data from both years are presented together with projections, through 1985, calculated from the increase in vehicle miles traveled by catalyst equipped cars and the mandatory phase-down in the sulfur content of unleaded gas. These projections will be compared with those derived from the GM/EPA Sulfate Dispersion Experiment.

INTRODUCTION

The catalytic converters with which most 1975 and later light-duty vehicles and trucks are equipped have been found to cause the oxidation of sulfur dioxide (SO_2) to sulfate in exhaust gases. While almost all forms of sulfate are considered to be deleterious to both health and visibility, sulfuric acid mist is of particular concern because of its irritant effect on respiratory tract membranes. In the atmosphere, many sulfates are deliquescent, so they readily absorb water vapor and grow to light scattering size. Also, since sulfates are particulates, they must be considered in any control strategy developed to meet ambient air quality standards for total suspended particulate matter. Thus, directly or indirectly, sulfates affect three ambient air quality standards: sulfate, visibility and total particulate. Additionally, the health hazard of certain sulfates cannot be ignored.

A baseline study was conducted by Rockwell International, Air and Industrial Hygiene Laboratories (California), California Department of Health, and the Environmental Protection Agency (EPA) along the San Diego freeway during 1974. The study took place before the advent of catalyst equipped vehicles. It concluded that sulfate emissions from noncatalyst equipped automotive sources were negligible (1). A brief California Air Resources Board (ARB) dynamometer study had indicated that sulfate emissions from catalyst equipped

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cars were many times greater than from previous years' models, although measurable sulfate emissions from pre-1975 vehicles were detected. It thus became of primary importance to measure sulfate emissions in traffic from catalyst equipped vehicles and to evaluate the health and atmospheric implications of any increase in sulfate concentrations. This report briefly presents the sampling procedures and analytical methods and discusses the increases in sulfate concentrations that might be attributable to catalyst-equipped vehicles.

METHODS

SAMPLING

The ARB has sampled for sulfate along both the Hollywood and San Diego Freeways. In May 1975, sites on the east and west sides of the San Diego Freeway, between Santa Monica and Wilshire Boulevards, were placed in operation. The "east" site is about 50 feet from the freeway; the "west," or background site, about 800 feet (Figures 1, 2, 3). During 1976 sampling was discontinued at the Hollywood Freeway; only the San Diego Freeway site is currently in operation.

Site selection was governed by several criteria, including: (1) proximity to freeway so as to measure sulfate emissions as directly as possible before they diffused completely into the ambient atmosphere; (2) prevailing wind direction perpendicular to the freeway; (3) low background levels of pollutants due either to direct emissions or to meteorological or photochemical processes; and, (4) high traffic counts on the freeway for several hours per day. The San Diego Freeway site meets these criteria well, the Hollywood Freeway site less well. At the ARB sites, twelve 2-hour particulate samples are taken every Tuesday, Wednesday and Thursday. The laboratory's usual low volume procedure (47 mm Gelman triacetate filters, flow rate ca. 4 cfm) is followed (2).

ANALYSIS

Sulfate and lead (Pb) are analyzed by X-ray fluorescence (XRF) (3). Although several other elements are detected by this technique, none is usually present in sufficient quantity to be reliably estimated on a day-to-day basis. Analyses have been completed for samples taken through January, 1977. The laboratory reports as "sulfate" all sulfur compounds detected by XRF, although the instrument determines sulfur as such regardless of whether it is present as sulfur, sulfate, sulfide or any other form. A comparison of XRF results with those obtained by a standard wet chemical sulfate analysis showed the XRF values to be approximately 30% higher. Data presented here are corrected for this disparity.

Aerometric data obtained at the San Diego East site consist of oxidant, carbon monoxide (CO), sulfur dioxide (SO_2), oxides of nitrogen (NO_x), wind speed and direction, hydrocarbons, relative humidity, temperature, UV intensity and b_{scat}. No aerometric data are obtained at the reference site (San Diego West).

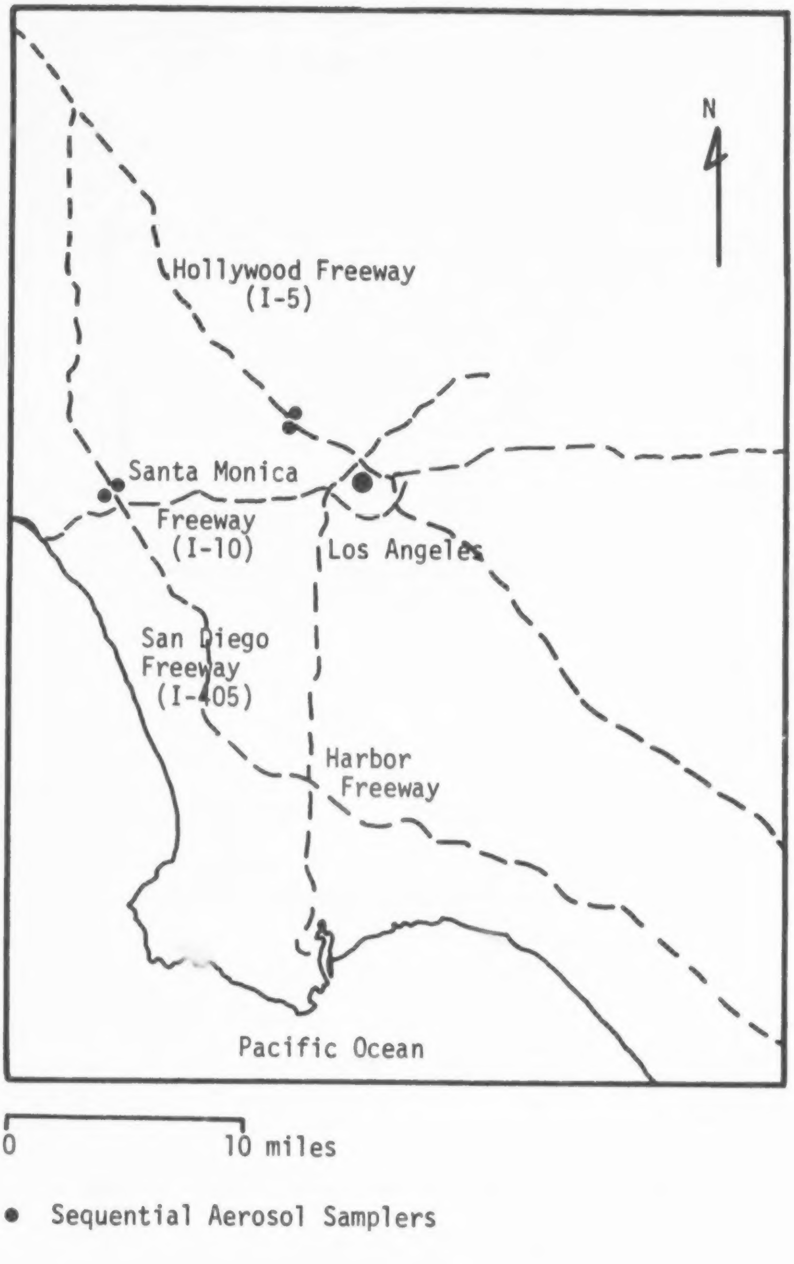
N
Hollywood Freeway
(I-5)
Santa Monica
Freeway
(I-10)
Los Angeles
San Diego
Freeway
(I-405)
Harbor
Freeway
Pacific Ocean
0
10 miles
● Sequential Aerosol Samplers

Figure 1. Sampling sites-ARB freeway sulfate study.

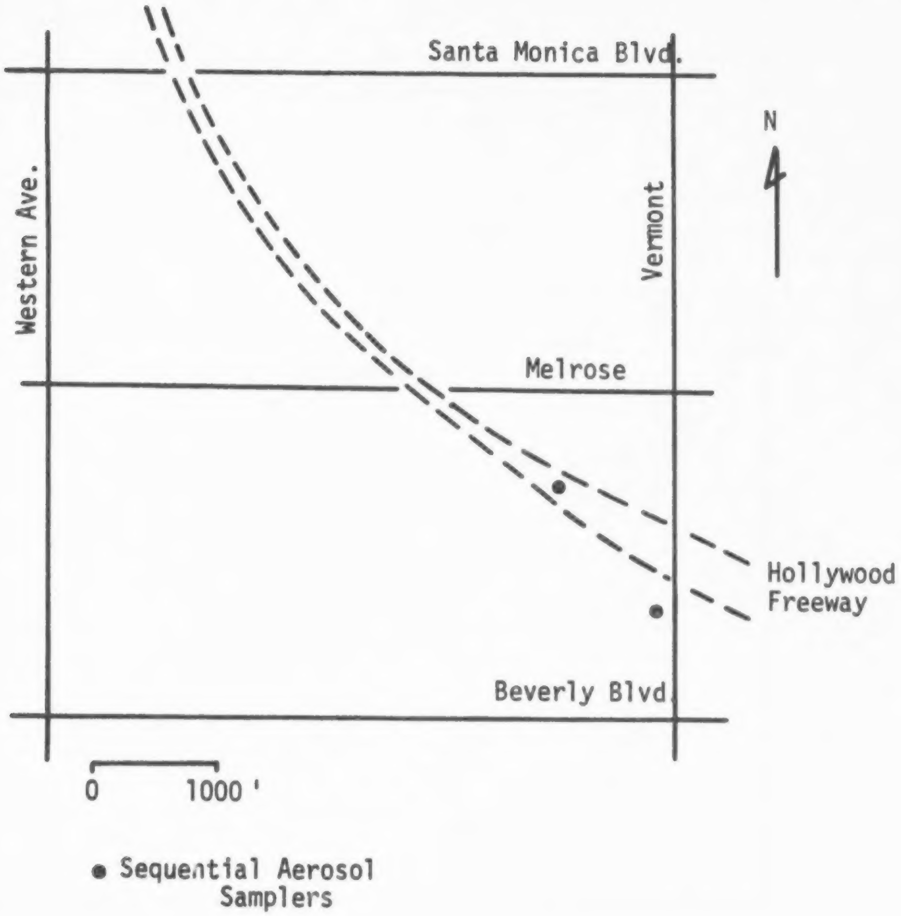
Santa Monica Blvd.
N
Western Ave.
Vermont
Melrose
Hollywood Freeway
Beverly Blvd.
0
1000'
● Sequential Aerosol Samplers

Figure 2. Sampling site Hollywood freeway.

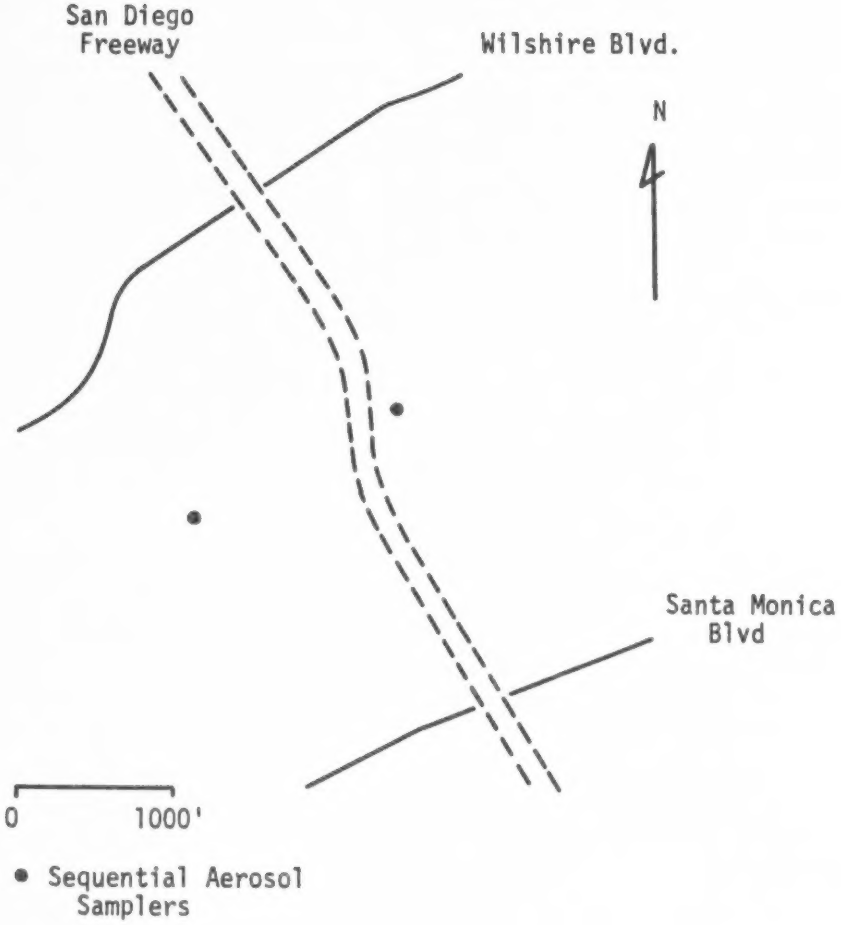
San Diego Freeway
Wilshire Blvd.
N
Santa Monica Blvd
0
1000'
● Sequential Aerosol Samplers

Figure 3. Sampling locations San Diego freeway.

RESULTS

Diurnal sulfate concentrations at the San Diego Freeway-East and -West sites for the Fall of 1975 are shown in Figures 4 and 5. The average corrected monthly differences (East vs. West), as measured and shown in Figure 6, were 1.3 μg/m^3 in August; 1.5 in September; 1.1 in October; and 0.9 in November. There was a substantial diurnal variation in sulfate concentrations. Maximum monthly differences (East vs. West) for any 2-hour interval of the day, for example the 10:00 - 12:00 a.m. period, averaged close to 3 μg/m^3, usually during midday. Differences were 2.6 in August; 3.7 in September; 3.0 in October; and 2.3 in November. The differences seemed to be a function of traffic count, freeway traffic speed, and wind direction and speed. During any single 2-hour sampling period, differences exceeding 5 μg/m^3 were common, and differences near or above 7 μg/m^3 were not unusual. (The largest single value was 7.5 μg/m^3). On occasion, differences averaged over an integrated 24-hour period exceeded 3 μg/m^3. "Normalized" sulfate differences, incorporating wind speed and direction, are shown in Figure 7.

Results obtained during the Fall of 1976 are not directly comparable with the 1975 results because statistical analyses reveal that week-to-week variations in 1975 were not random. The average monthly differences, west to east, for August through November, 1976 as shown in Figure 8 were as follows:

August	*2.1*
September	*1.4*
October	*1.3*
November	*1.1*

These figures take into account the signs of the differences. "Normalized" values are shown in Figure 9. Although the monthly averages show little apparent change, 1975 vs 1976, the number of two-hour periods when differences approximated or exceeded 10 μg/m^3 was substantially greater in 1976. The largest 24-hour difference found in 1976 was 7.5 μg/m^3. Concentrations of primary pollutants (including SO_2) and oxidant were invariably low.

The data obtained at the Hollywood Freeway during 1975 are presented graphically in Figures 10 through 12. Analyses not presented here suggest that incremental sulfate values there are somewhat smaller than at the San Diego Freeway site.

PROJECTIONS

Calculations based on the estimated number of catalyst-equipped vehicles in Los Angeles County (R.L. Polk and Co. Statistics) and the average number of miles a car travels annually, depending on its age (4), indicate that catalyst-equipped cars accounted for about 16.4% of the vehicle miles traveled (VMT) during the Fall of 1975. If sales of light-duty vehicles in the next several years equal those for the 1974 model year, and if the current mileage vs. age figures hold true, the ratio of miles traveled by catalyst-equipped vehicles, compared to the 1975 mileage, would be about 2.16 by November, 1976; 3.04 by November, 1977; and 3.78 by November, 1978.

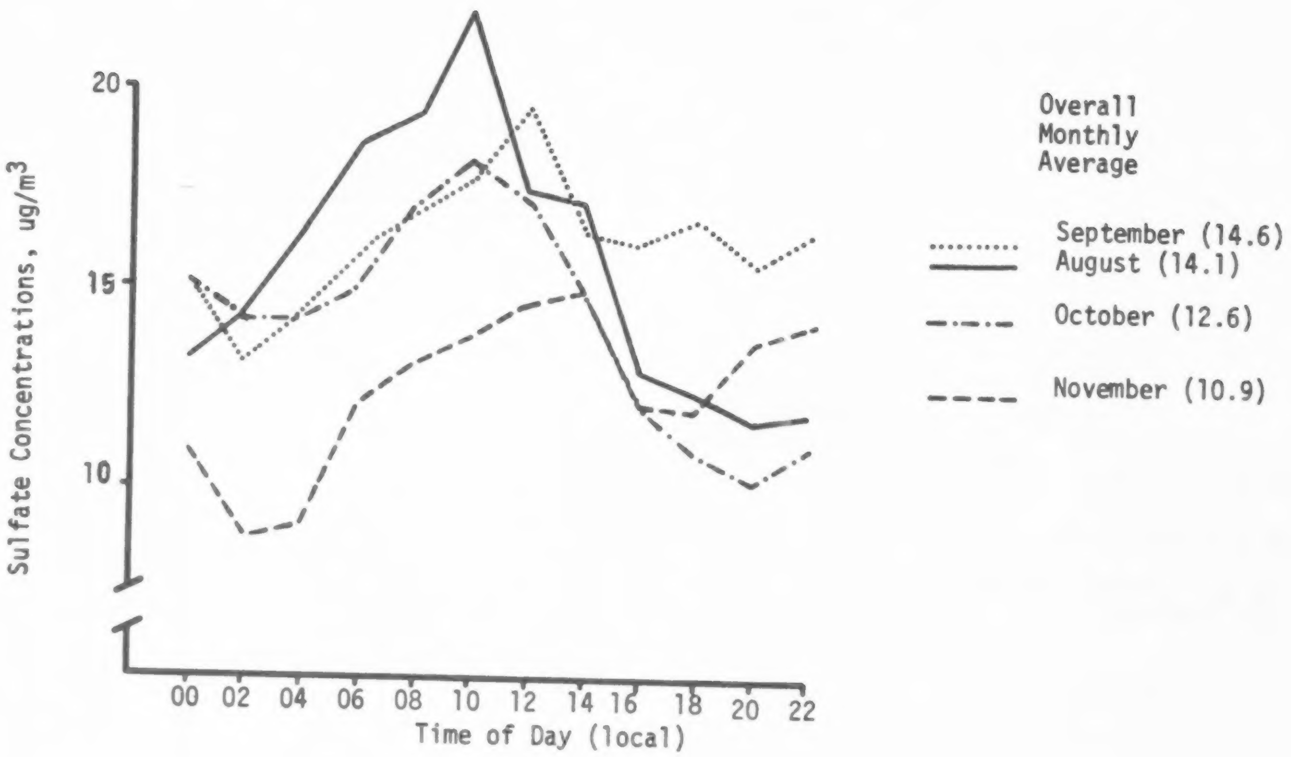

Figure 4. Diurnal variations in sulfate concentrations, San Diego freeway-east (SDE), 1975.

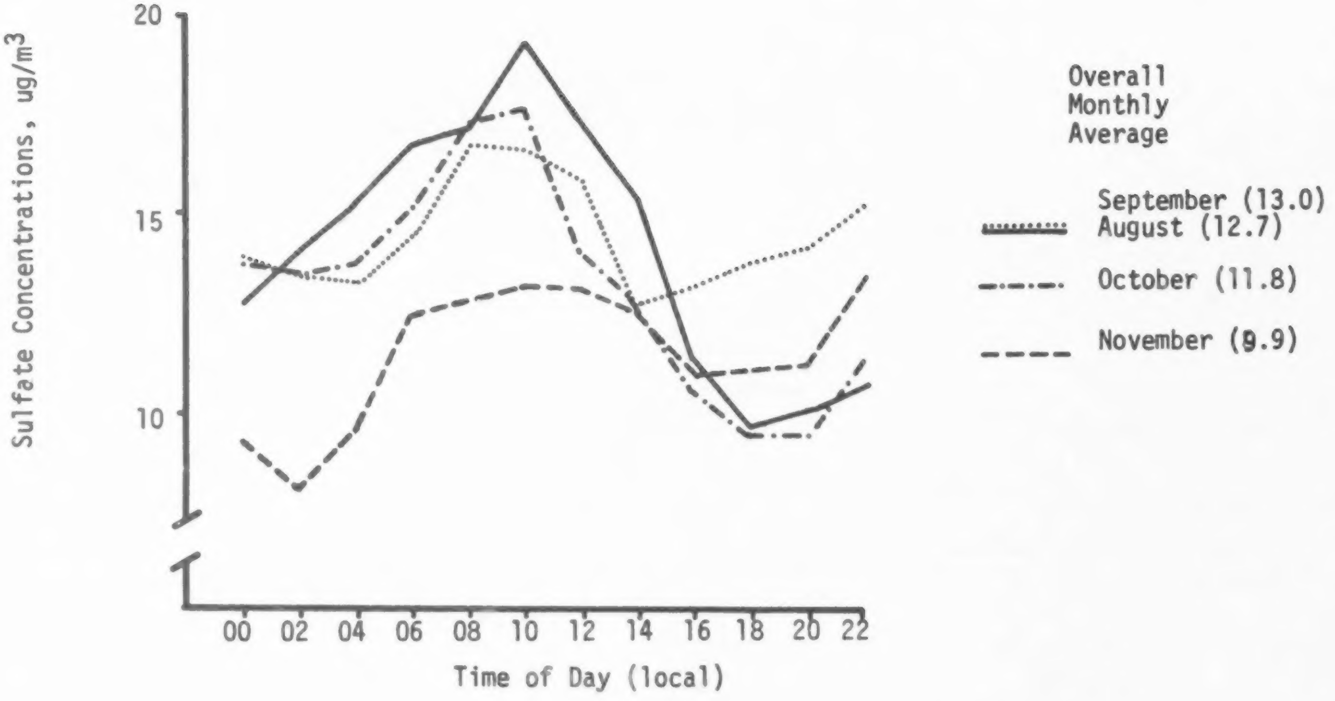

Figure 5. Diurnal variations in sulfate concentrations, San Diego freeway-west (SDW), 1975.

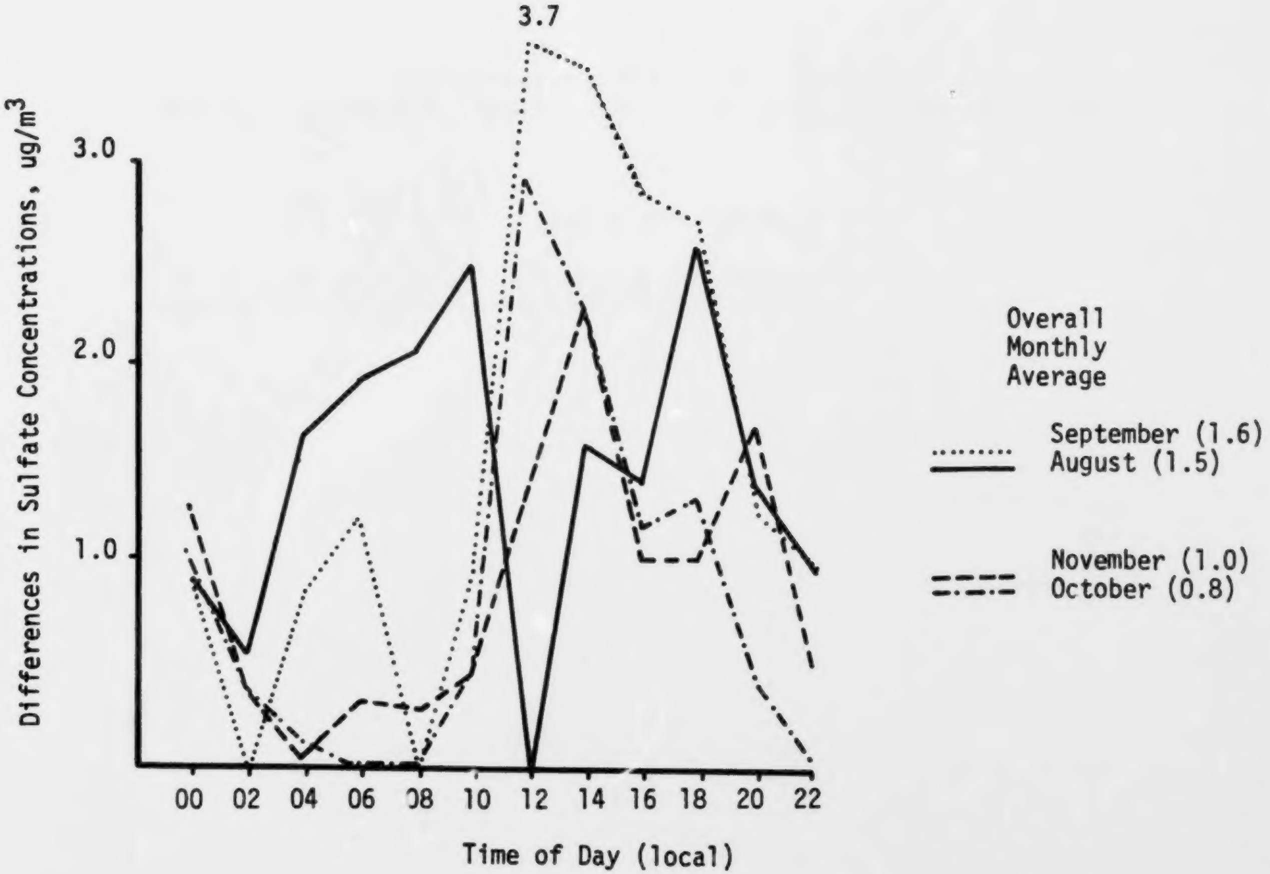

Figure 6. Differences in diurnal variations in sulfate concentrations, SDE vs SDW, 1975.

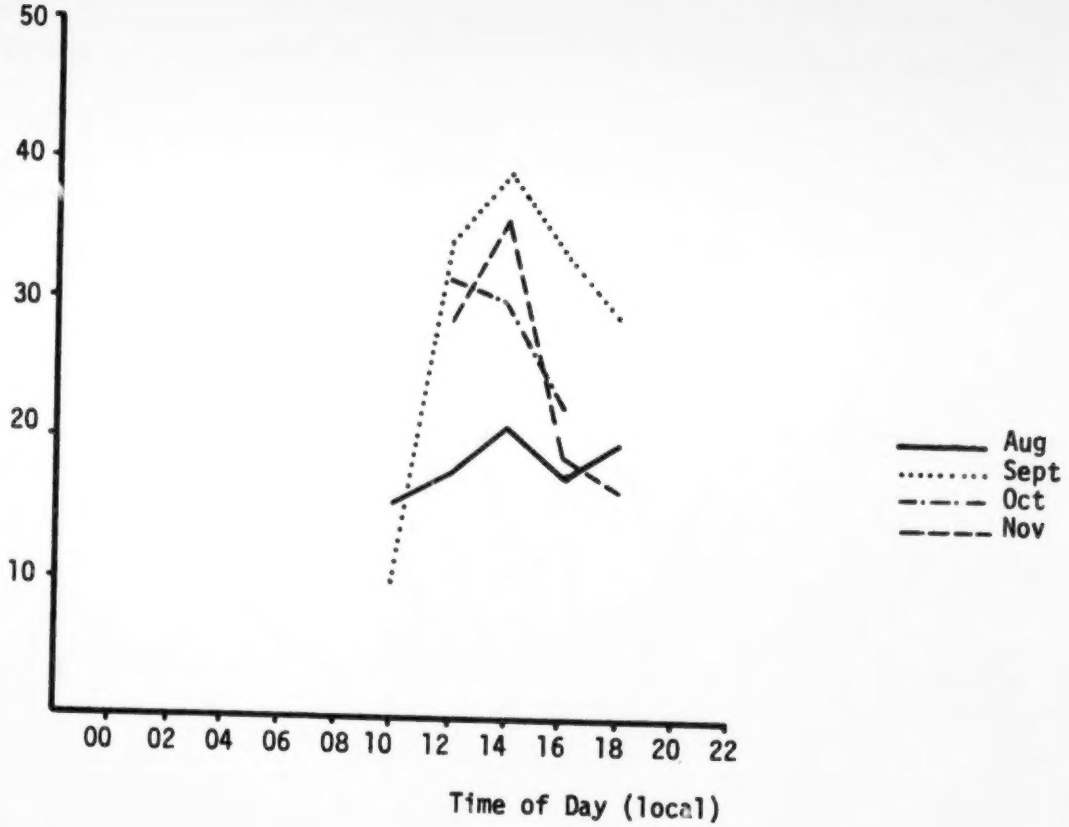

Figure 7. "Normalized" diurnal variations in differences in sulfate concentrations, SDE vs SDW, 1975.

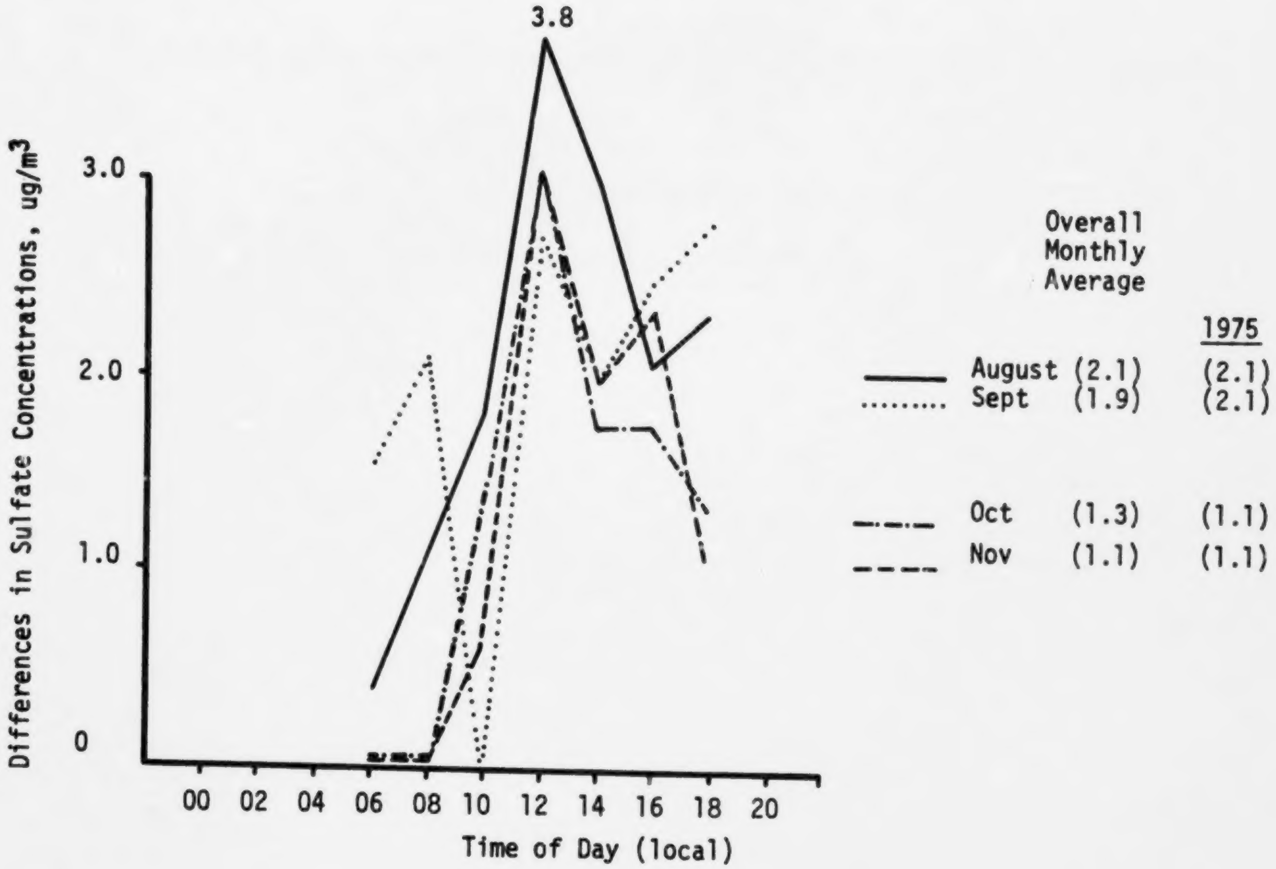

Figure 8. Differences in diurnal variations in sulfate concentrations, SDE *vs* *SDW, 1976.*

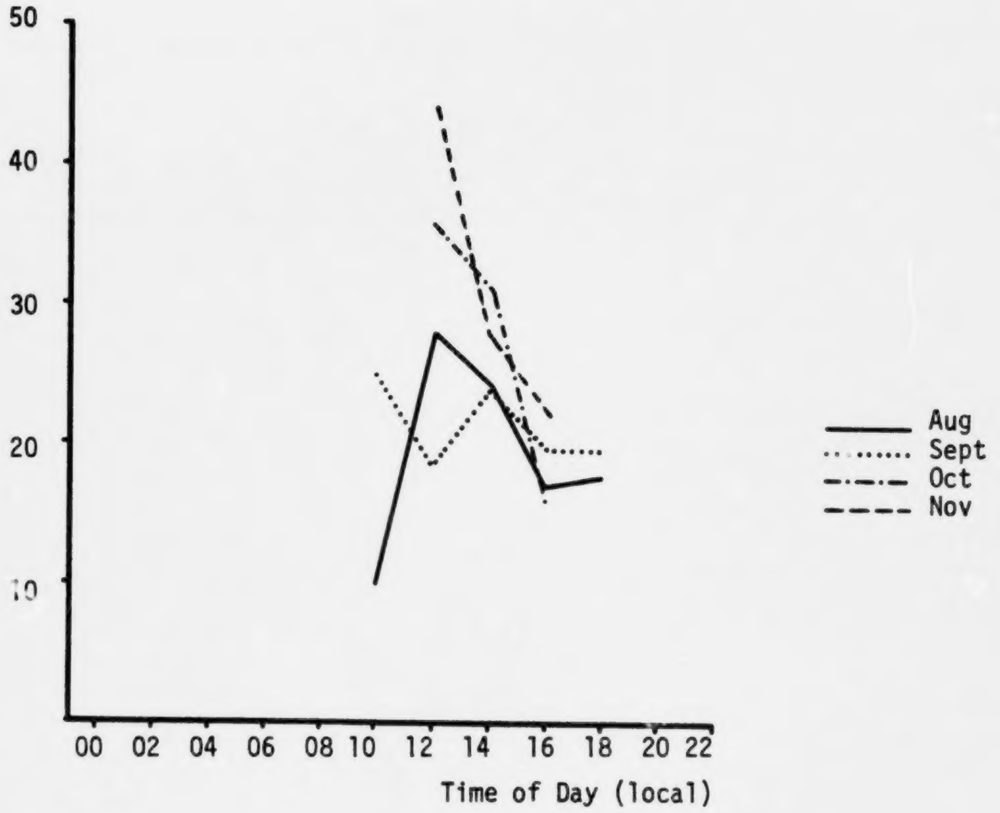

Figure 9. "Normalized" diurnal differences in sulfate concentrations SDE vs SDW, 1976.

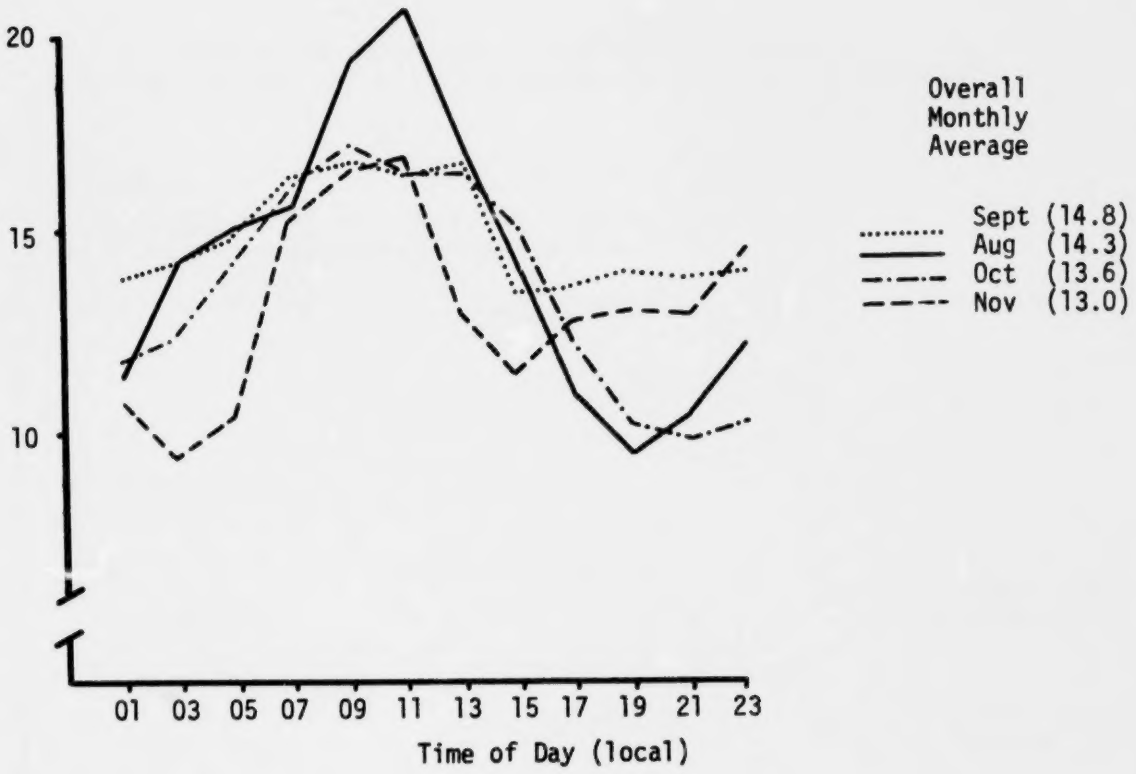

Figure 10. Diurnal variations in sulfate concentrations, Hollywood freeway (HF), 1975 monthly averages.

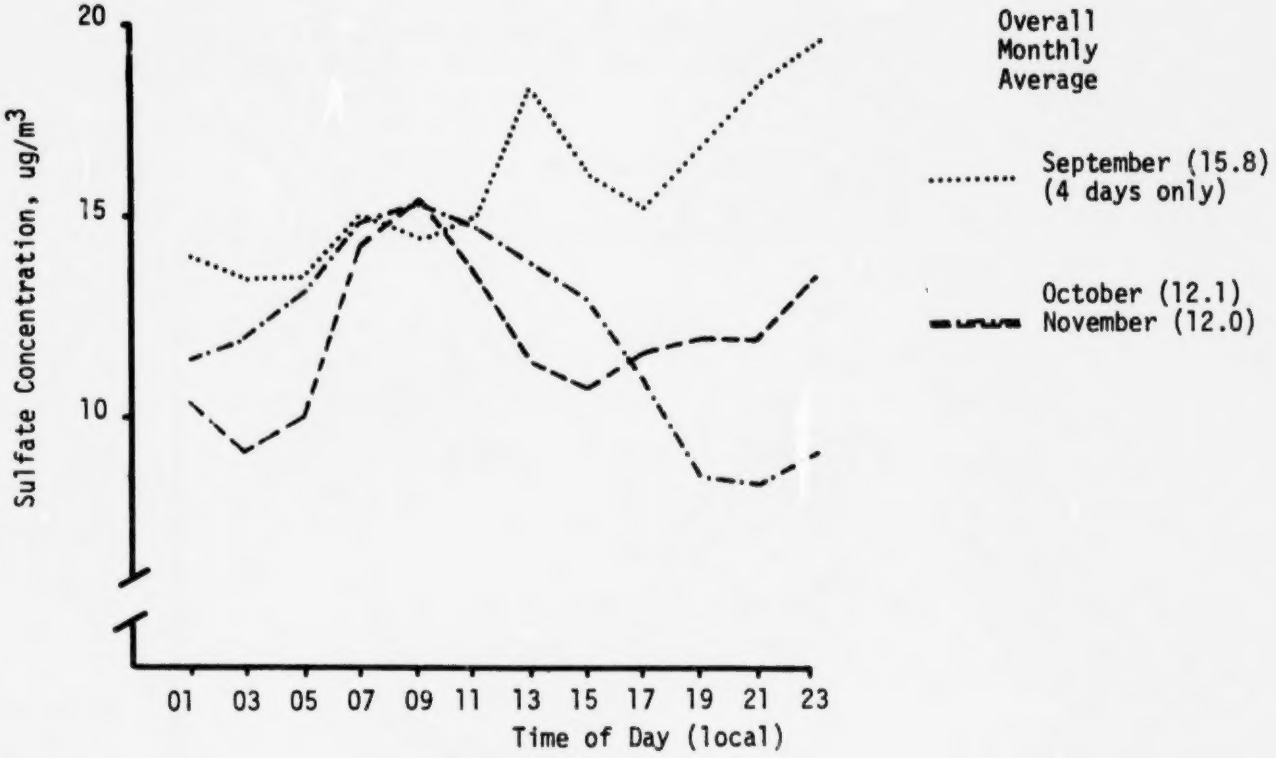

Figure 11. Diurnal variations in sulfate concentrations, Hollywood freeway reference (HFR), 1975 monthly averages.

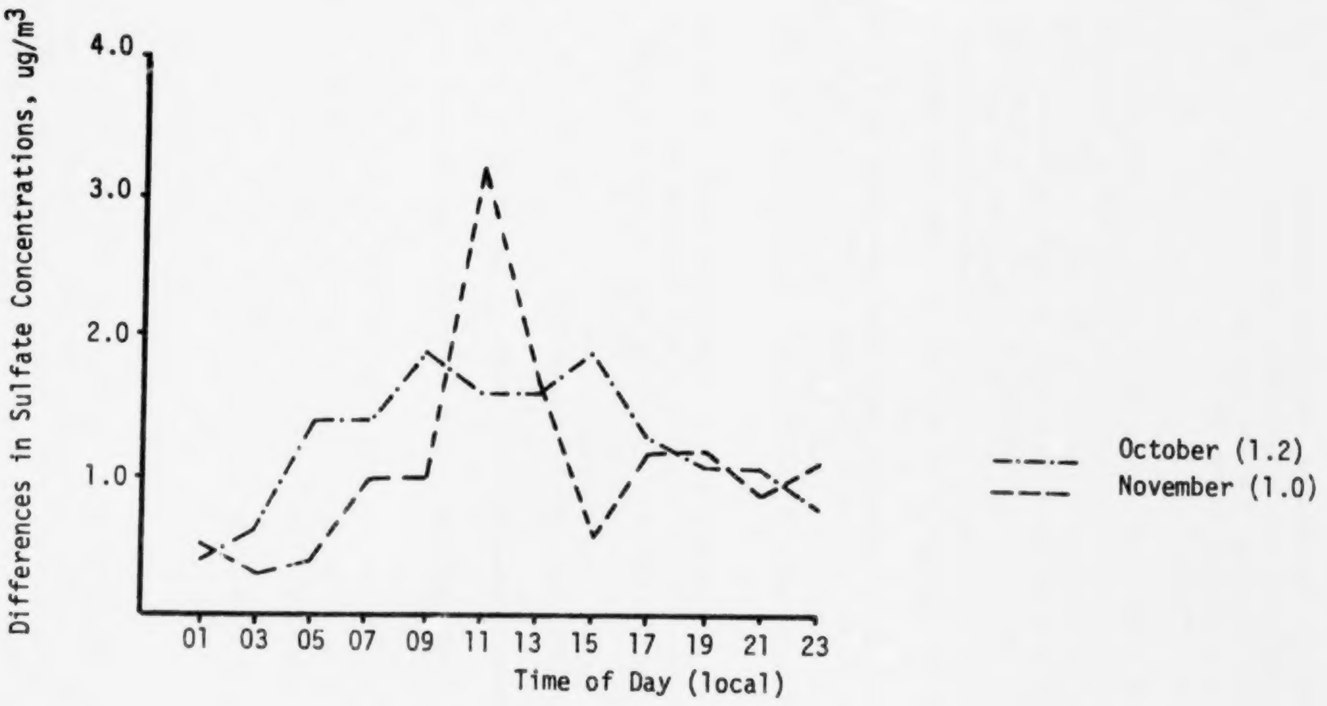

Figure 12. Diurnal differences in sulfate concentrations HF vs HFR, 1975.

If the average sulfur (S) content of lead-free gasoline sold in the Los Angeles area remains 270 ppm, its reported current weighted average (5), then based on the San Diego freeway data, the sulfate contribution from the catalyst-equipped vehicles would approximate those shown in Table I, assuming no changes in engine or catalyst performance.

Since about 95% of all VMT is accumulated by cars that are less than ten years old, and 48% by cars sold in the last three model years, the amount of VMT by catalyst-equipped cars will eventually be approximately six times the VMT by the 1975 cars. Long range projections are usually hazardous, but the current data suggest that in 1979 S contributions would be 4.4 times the 1975 values, assuming that the S content of gasoline remained at 270 ppm. Further increases in VMT after 1980 would not be offset by a lower S content of gasoline unless the limit of 300 ppm after January 1, 1980 were lowered.

In 1980, for example, the S increment from gasoline would be 5.0 times the 1975 value. In 1981 it would be 5.5 times and in 1982, 6.0 times. From 1985 on, the S contribution would level out (using the conservative assumptions stated earlier) at about 6.8 times the 1975 level. Projections for each year are shown in Table II.

These projections agree remarkably well with those which can be derived from the General Motors (GM)/EPA Sulfate Dispersion Experiment (6). In that study the traffic count was 10,920 cars every two hours. The S content of gasoline averaged 300 ppm. The average sulfate increase was 8 $\mu g/m^3$ and the maximum increase was 16 $\mu g/m^3$. The maximum 24-hour traffic count on the San Diego Freeway averaged 19,250 cars per 2-hour period, and the maximum 2-hour count was 28,420. Adjusting for traffic count, the maximum 24-hour daily average increase in sulfate concentrations, based on the GM data, would be $14.1\ \mu g/m^3\ \frac{(19,250 \times 8)}{(\ 10,920\ )}$. The maximum 2-hour concentration increase would be $41.6\ \mu g/m^3\ \frac{(28,420 \times 16)}{(\ 10,920\ )}$. Our projections are 14.5 and 36.3, respectively. During the 14 hour period from 0600-2000 the traffic count on the San Diego Freeway averages 26,100 cars per 2-hour period; the GM data then project to $19.1\ \mu g/m^3$ increase during this period $\frac{(26,100 \times 8)}{(\ 10,920\ )}$.

SUMMARY

The laboratory has sampled at both the Hollywood and San Diego Freeways in order to determine the increase in atmospheric sulfate caused by sulfate emissions from catalyst equipped vehicles. Sampling began in May 1975 but background data at both sites have been available only since September, 1975. Data from the San Diego Freeway locations are considered to be more reliable than those from the Hollywood Freeway.

A freeway sulfate contribution is evident at each site. The maximum contribution seems to occur at midday when traffic counts are high, traffic is moving rapidly, and a sea breeze is blowing across the freeway.

TABLE I. PROJECTED SULFATE CONTRIBUTION ($\mu g/m^3$) FROM CATALYST-EQUIPPED VEHICLES

Year	Monthly Average	Maximum in 24 hours	Maximum in 2 hours
1976 (November)	2.8	6.4	15.3
1977 (November)	3.9	8.7	21.6
1978 (November)	4.8	11.1	26.8

TABLE II. INCREMENTAL SULFATE EMISSIONS FROM CATALYST EQUIPPED VEHICLES, 1979-85, RELATIVE TO 1975 (S CONTENT OF GASOLINE ASSUMED TO BE 270 PPM)

Year	Catalyst-Equipped Vehicle VMT (Billions)	Ratio to 1975 Catalyst-Equipped Vehicle VMT	Sulfate Emission Increase, (1975=1.00)
1979	23.49	4.43	4.4
1980	26.68	5.03	5.0
1981	28.94	5.46	5.5
1982	31.90	6.02	6.0
1983	34.04	6.42	6.4
1984	35.77	6.75	6.7
1985 on	36.24	6.84	6.8

If the currently observed increment in sulfate values continued to be proportionate to the vehicle miles traveled by catalyst equipped cars, by 1985 the maximum 2-hour concentration at the freeway would increase by about fourfold, the maximum 24-hour increase would be a significant part of the ambient air quality standard, and the monthly average would increase by about 7.7 $\mu g/m^3$. *These predictions agree well with those that may be derived from the GM/EPA Sulfate Dispersion Experiment.*

ACKNOWLEDGMENT

The authors are indebted to Marilyn Smithson, Eric Fujita and Sidney Shimabukuro for sample collection, and to Arthur Heath and Dr. Donald W. Davis for analyses.

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SUMMARY OF LACS CONTINUOUS DATA

Gary F. Evans and Charles E. Rodes

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

Continuous measurements have been made in the Los Angeles Catalyst Study for wind direction and speed, temperature, relative humidity, traffic count and speed, and upwind and downwind concentrations of carbon monoxide, nitric oxide, nitrogen dioxide, total sulfur and ozone. Each of these variables is reported in hourly values. The frequency of occurrence of wind directions and associated speed are discussed along with the diurnal and seasonal patterns of wind direction, wind speed, temperature and relative humidity. Hour-of-day patterns in count and speed , presented for Northbound and Southbound traffic data, have only been collected on-site since September 1976; estimates of the total volume at the monitoring site for the past five years have been obtained from the California Department of Transportation. Hourly pollutant concentrations at upwind and downwind sites and the cross-freeway difference are examined in relation to wind direction, wind speed, hour-of-day, season, traffic volume and traffic speed. Emphasis in these comparisons is placed on carbon monoxide since it is a primary and non-reactive pollutant. Finally, long-term trends in the concentrations of all continuously monitored pollutants are discussed.

INTRODUCTION

The location of the sampling sites for the Los Angeles Catalyst Study (LACS) is shown in Figure 1. The four permanent sites are situated along a line perpendicular to the San Diego Freeway with two sites on either side. Through this part of the Los Angeles basin, the freeway runs parallel to the Pacific Ocean (i.e., Southeast to Northwest) at a distance of approximately four miles inland. The freeway perpendicular, serving as the site line, occurs at 235^0 (i.e., in the Southwest octant).

Figure 2 is an aerial view of the Veterans Administration Hospital property on which the LACS sites are located. The figure indicates the positions of permanent sites A and B on the ocean (or "upwind") side of the freeway and C and D on the opposite (or "downwind") side. All of the continuous monitoring equipment is located at site A (100 feet upwind of the freeway) and/or site C (25 feet downwind). Also shown in the figure is temporary site A^1 which is located in an open field some 700 feet from the freeway on the upwind side. A carbon monoxide (CO) analyzer was operated at

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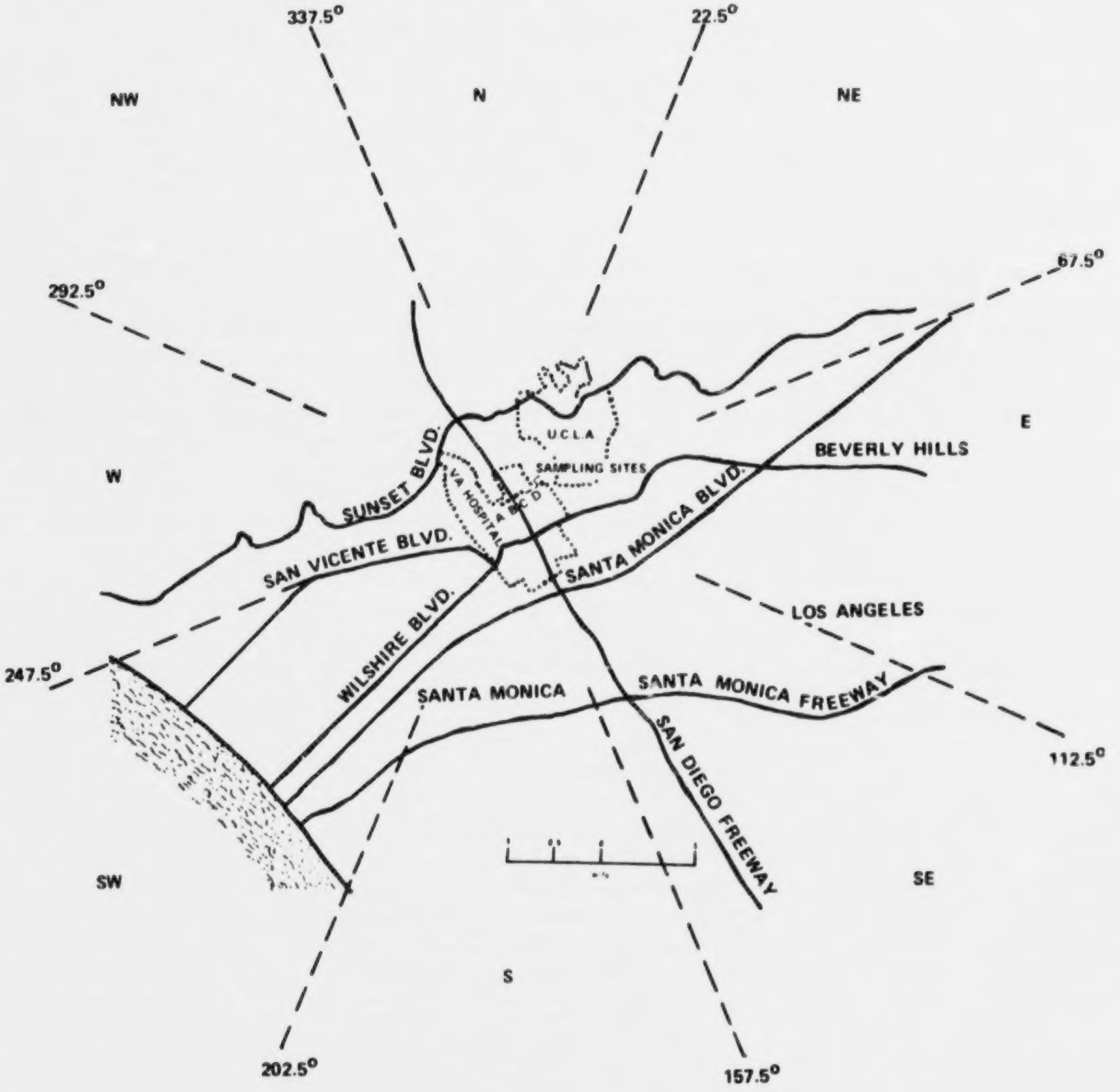
337.5°
22.5°
NW
N
NE
67.5°
292.5°
UCLA
E
SAMPLING SITES
BEVERLY HILLS
W
SUNSET BLVD.
VA HOSPITAL
A B C D
SAN VICENTE BLVD.
SANTA MONICA BLVD.
LOS ANGELES
WILSHIRE BLVD.
247.5°
SANTA MONICA
SANTA MONICA FREEWAY
SAN DIEGO FREEWAY
112.5°
SW
SE
S
202.5°
157.5°

Figure 1. Site location in Los Angeles.

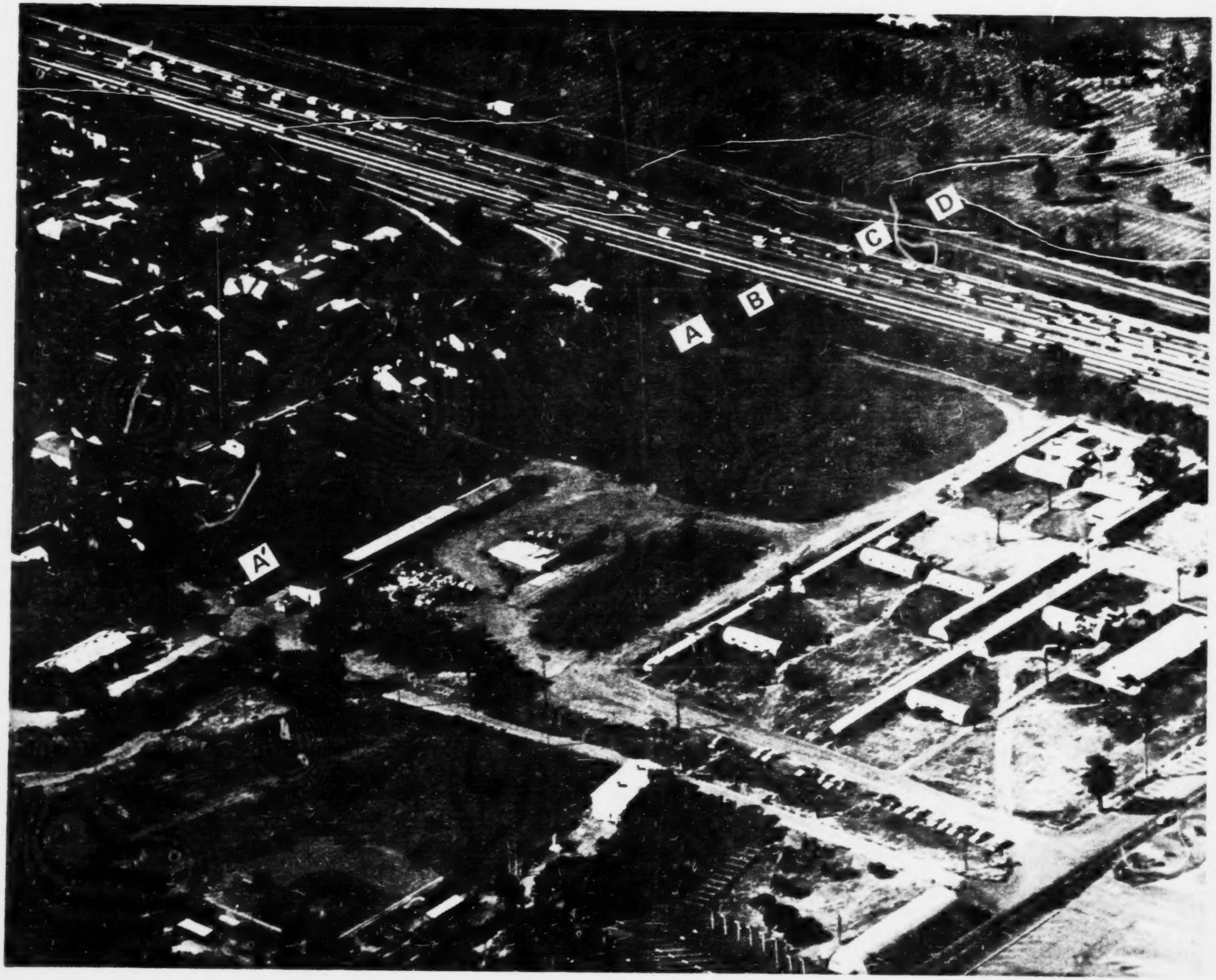

Figure 2. Aerial view of sampling sites.

site A[1] during the summer of 1975 in an effort to determine whether permanent site A adequately reflects true background concentrations.

Table I lists the variables in the LACS which are continuously monitored and reported as hourly averages. The sampling location, method and period of data coverage are shown for each continuously monitored variable.

METEOROLOGICAL DATA

Wind direction and speed have been continuously monitored since the beginning of the LACS (June 1974) by means of a Climet anemometer located at site A at an elevation of 10 meters. During the first six months of the study, simultaneous readings of wind direction and speed were collected with an MRI anemometer at site D at an elevation of 3 meters. Comparison of the data from the two systems showed that the wind direction information was essentially equivalent and that wind speeds recorded at site A, though highly correlated with corresponding readings at site D, were approximately 3 times as great due to the difference in elevation. As a result of the favorable comparison, the anemometer at site D was discontinued in December 1974.

Figure 3 depicts the distribution of occurrences and the associated average wind speed as a function of wind direction. Wind direction strip charts are reduced to hourly averages and reported to the nearest ten degrees. Thus, there are 36 possible values for wind direction plus the classification 'calm' (denoted by zero) which is used for any hour for which the accompanying wind speed is less than one mile per hour. The lower curve in Figure 3 is a frequency distribution of all the wind direction data collected at site A since the beginning of the study. It was plotted by tabulating the number of hours of occurrence for each possible wind direction, dividing by the total number of hours for which valid wind direction data are available (about 18,000 hours) and expressing the quotients as percentages. The upper curve is the average wind speed over all hours for which the winds were from the indicated direction.

Prevailing wind direction was one of the prime considerations involved in the selection of a suitable site for the LACS. Areas of the Los Angeles basin which are close to the ocean are characterized by an alternating pattern of onshore (or "seabreeze") winds during the daylight hours and offshore (or "landbreeze") winds during the dark hours. Thus, it was felt that a major freeway running parallel and near to the ocean would provide the desirable property of prevailing winds which were perpendicular to the freeway for a large portion of almost every day. Such a wind pattern would enable the detection of the freeway contribution to ambient levels of air pollutants by differencing simultaneous measurements taken upwind and downwind of the freeway.

As shown in the lower curve in Figure 3, wind direction at the LACS site does follow a bimodal distribution with two distinct patterns: a seabreeze pattern centered in the Southwest with tails in the South and West and a somewhat more diffuse landbreeze pattern centered in the North with tails in the Northwest and Northeast. The upper curve in Figure 3 shows that the seabreeze is accompanied by the highest wind speeds.

TABLE I. INVENTORY OF CONTINUOUS DATA

Variable	Sampling Location	Sampling Method	Sampling Period
Wind Direction/Speed	Site A (10 m.)	Climet Anemometer	June 74 - present
Wind Direction/Speed	Site D (3 m.)	M.R.I. Anemometer	June 74 - December 74
Temperature/Dew Point	Site A (1 m.)	Thermistor/LiCl Detector	October 74 - present
Traffic Count/Speed	All lanes	Inductive Loop System	September 76 - present
Carbon Monoxide (CO)	Sites A & C (1 m.)	Nondispersive Infra-red	June 74 - present
Carbon Monoxide (CO)	Site A' (1 m.)	Nondispersive Infra-red	June 75 - September 75
Nitric Oxide (NO)	Sites A & C (1 m.)	Chemiluminescence	January 75 - present
Nitrogen Dioxide (NO_2)	Sites A & C (1 m.)	Chemiluminescence	January 75 - present
Ozone (O_3)	Sites A & C (1 m.)	Chemiluminescence	January 76 - present
Total Sulfur (S)	Sites A & C (1 m.)	Flame Photometric	May 75 - present

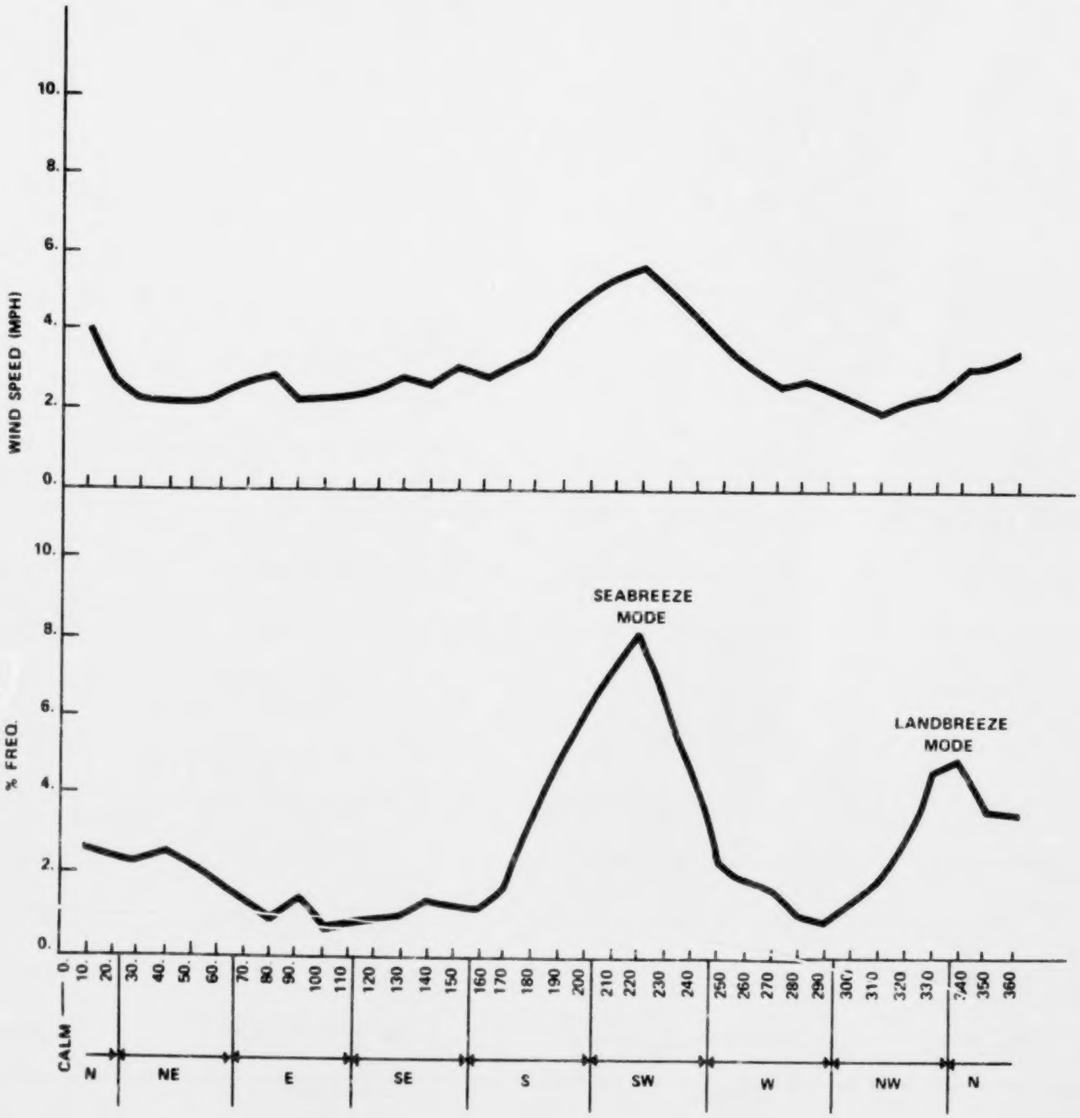

Figure 3. Percent frequency and speed by wind direction (all data).

Since the seabreeze mode (wind directions from the South, Southwest or West) provides the most favorable conditions for the detection of pollutant sources on the freeway, it is useful to look at the diurnal and seasonal patterns in the occurrence of winds from this sector. Figure 4 shows the percentage occurrence of seabreeze by hour-of-day for all summer months (defined as April through September, inclusive). In the early morning hours. winds are typically light and variable and are out of the seabreeze sector (S+SW+W) for only about 20% of all summer days. Following sunrise (about 7 a.m.) the wind pattern begins to shift into the seabreeze mode and from noon until 7 p.m. winds are nearly always from this favorable sector.

Since the LACS integrated samplers are operated on either a 24-hour basis (midnight to midnight) or a 4-hour basis (3-7 p.m.), the overall percentage occurrence of seabreeze for each of these intervals is shown in the figure (61% and 97%, respectively). This suggests that while the 4-hour afternoon sampling interval should provide a good measure of the freeway contribution to pollutant concentrations, the 24-hour interval will likely be an underestimate since the diurnal wind pattern is such that all sites will be impacted upon by the freeway during some portion of the day.

Figure 5 shows the diurnal pattern of seabreeze for winter months (October through March). While similar to the summer pattern, the figure shows that the period of favorable meteorology is of much shorter duration because there are fewer hours of sunlight. Overall, the seabreeze accounts for only 35% of winter hours and from 3-7 p.m. the percentage seabreeze is only 65%. Thus, it would appear that cross-freeway differences obtained from integrated samplers would be notably different between summer and winter seasons. The LACS integrated data are discussed in a separate report in these proceedings.

The diurnal pattern for temperature is shown in Figure 6 with separate curves for the summer and winter seasons. Temperature follows a symmetrical pattern reaching its peak in the early afternoon. The seasonal difference in temperature is not large (5°F overall average). Figure 7 provides the same information for percent relative humidity. Humidity reaches a minimum in the early afternoon and averages 5% higher in the summer season.

TRAFFIC DATA

The LACS traffic count and speed system became operational in September 1976. The system consists of inductive loops embedded in each of the ten lanes of the San Diego Freeway, and interface system to convert electric impulses from the loops to digital counts and a mini-computer located in the shelter at site C to store traffic count data on magnetic tape. Operating on a ten minute cycle, the system provides a total vehicle count for each lane and within each of six speed categories: 0-25, 25-35, 35-45, 45-55, 55-65 and greater than 65 miles per hour (mph). As of December 1976, only eight of the ten lanes of the freeway were open to traffic (four lanes Northbound and four lanes Southbound).

Every two weeks, the magnetic tape from the on-site computer is forwarded to Research Triangle Park, N. C. (RTP) where the data are reduced to hourly traffic volume and estimated average speed Northbound and South-

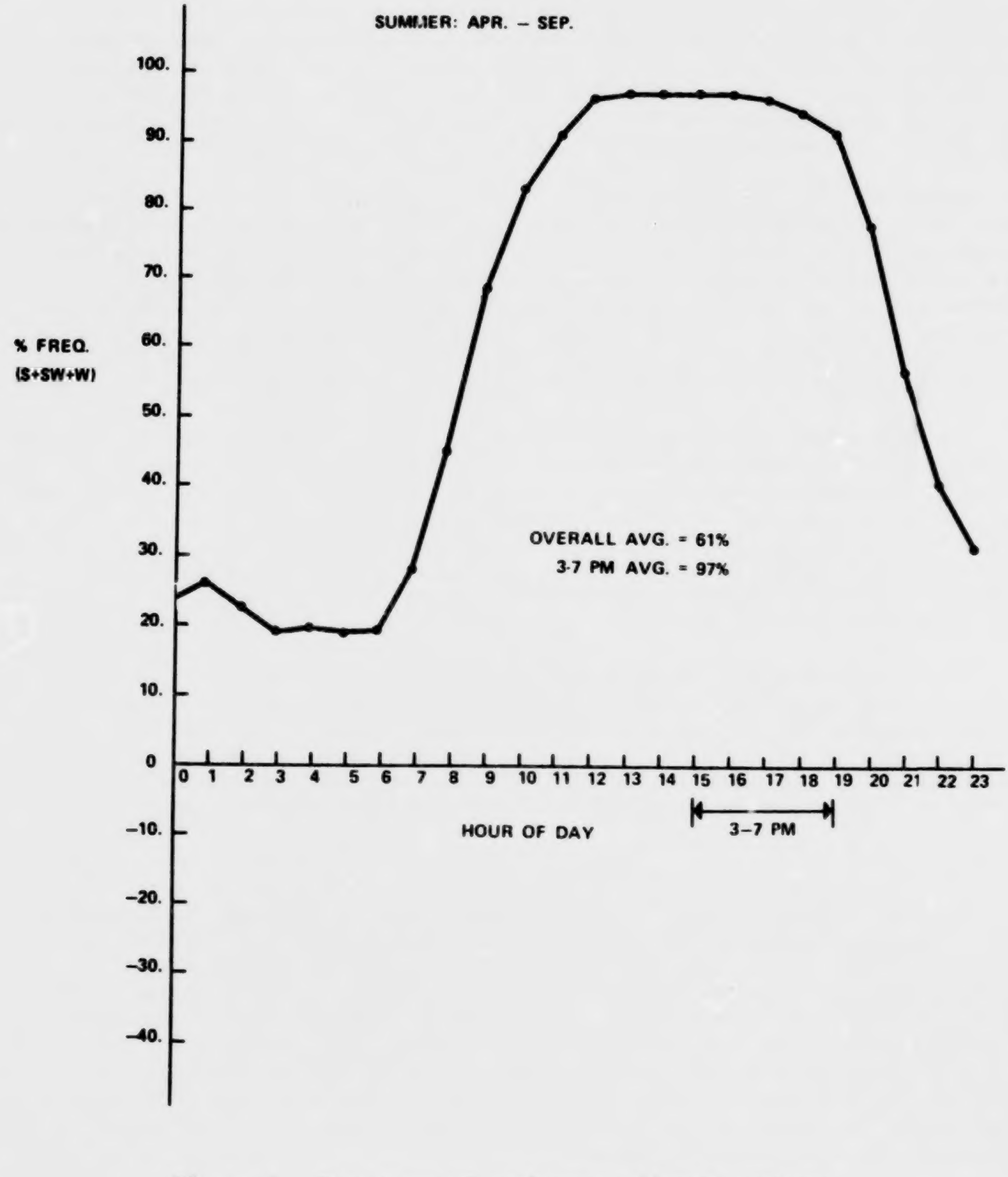

Figure 4. Frequency of seabreeze, diurnal pattern.

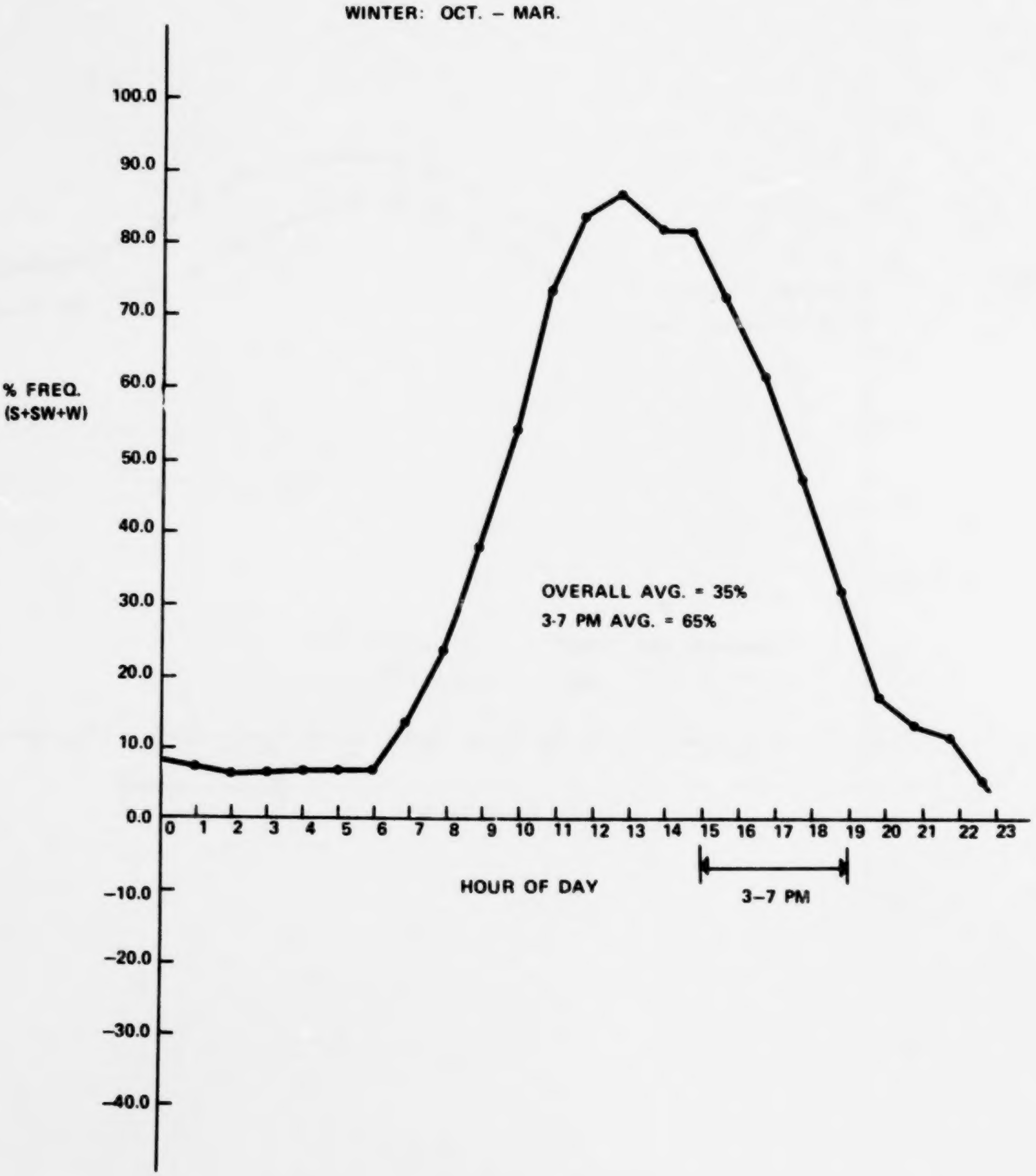

Figure 5. Frequency of seabreeze, diurnal pattern.

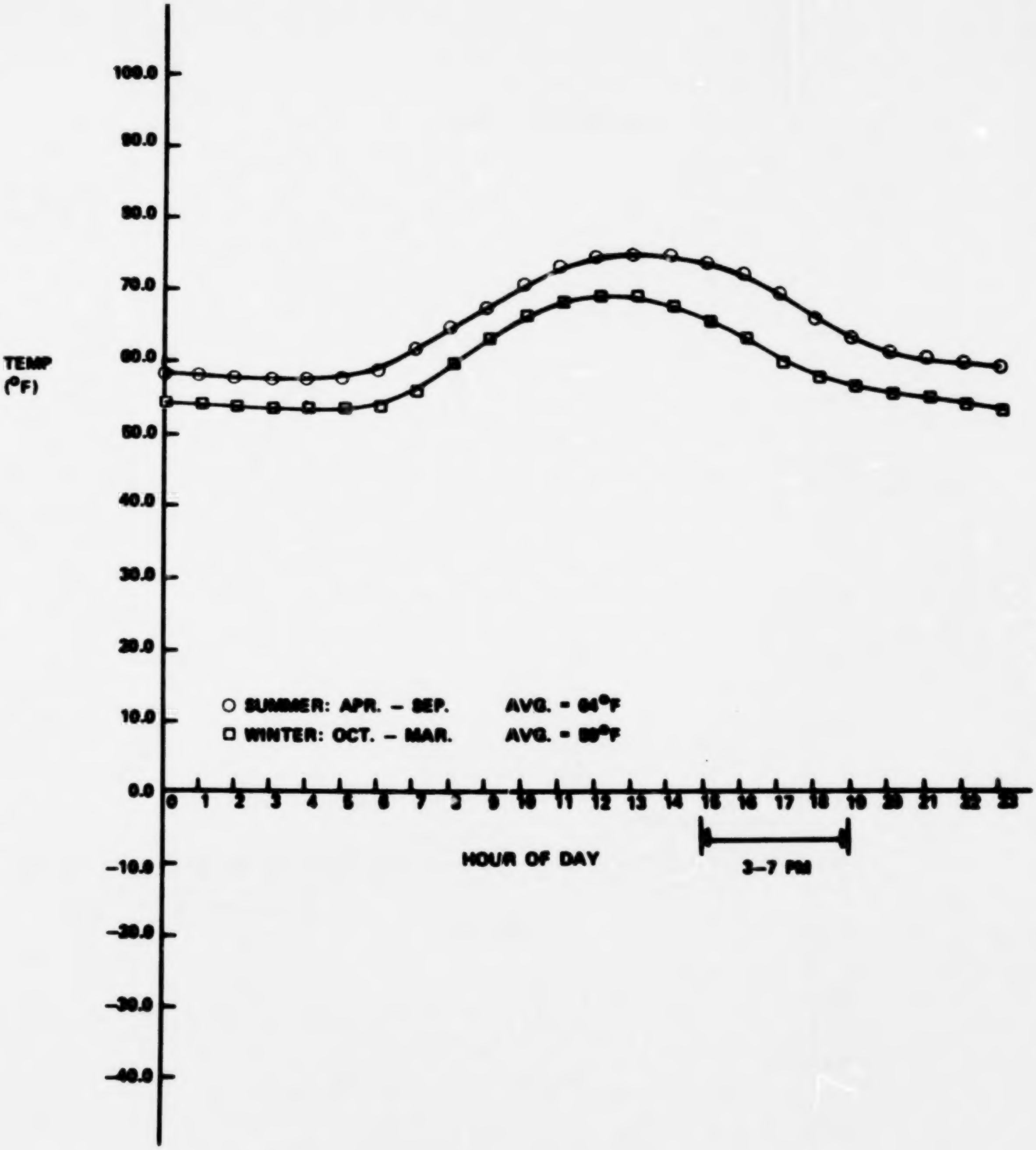

Figure 6. Temperature by hour.

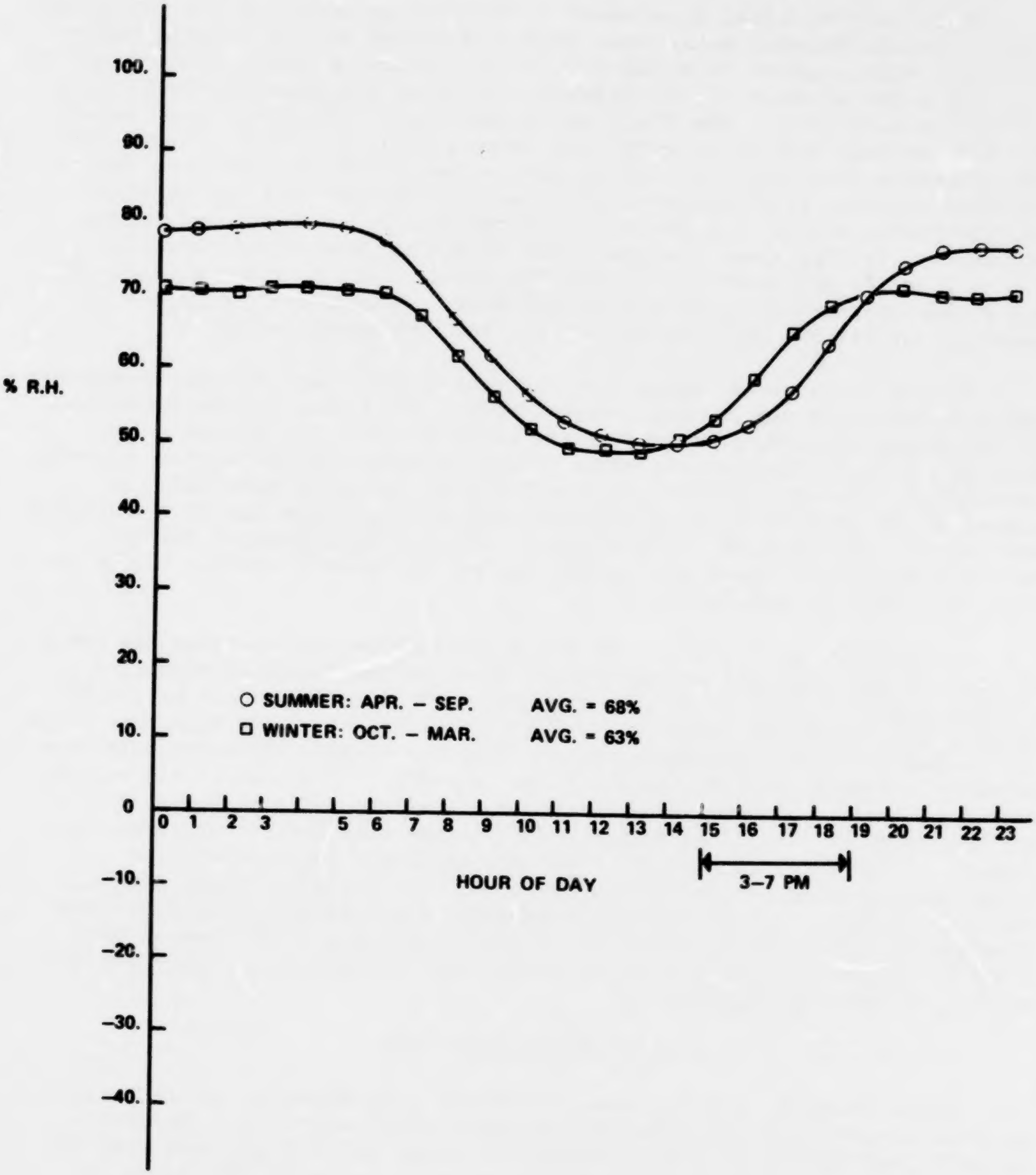

Figure 7. Relative humidity by hour.

bound. Figures 8-11 present the diurnal patterns for traffic count and speed composited over the period for which valid data are available (September through December 1976).

Since no statistical day-of-week differences appeared for the composited Monday through Thursday data, these days were pooled into an overall weekday composite which appears in Figure 8. Traffic volume follows a bimodal pattern reaching peaks at about 7 a.m. (morning rush hour) and again at about 4 p.m. (afternoon rush hour). The Southbound lanes exhibit the larger peak during the morning rush hour while Northbound lanes exhibit the larger peak during the afternoon rush hour. This phenomenon is consistent with the fact that the LACS location is Northwest of downtown Los Angeles; thus the weekday traffic burden shifts from Southbound in the morning to Northbound in the afternoon. Traffic speed averages about 55 mph but congestion causes it to dip to about 40 mph Southbound during the morning rush hour and to about 20 mph Northbound during the afternoon rush hour. Average traffic volume for weekdays was 191,500 vehicles per day for the four month period.

Figures 9, 10 and 11 present the diurnal traffic patterns for composited Fridays, Saturdays and Sundays, respectively. The Friday pattern is similar to the Monday-Thursday pattern with the exception that the afternoon rush hour is of longer duration. Overall traffic volumes for Fridays was 205,000 vehicles per day or 7 percent greater than that for other weekdays. As expected, the patterns for Saturday and Sunday do not show the characteristic morning and afternoon rush hour patterns, average speed remains fairly constant throughout the course of the day and the overall traffic volume is less than that for weekdays.

The quotient of traffic count and corresponding average speed has units of vehicles per mile and may be thought of as an instantaneous measure of traffic density. Figures 12 through 15 show the diurnal pattern of traffic density for composited weekdays (Monday through Thursday), Fridays, Saturdays and Sundays. It is interesting to note that the weekday afternoon rush hour produces a peak in traffic density which is nearly twice that of the morning rush hour period. It should be pointed out that the 3-7 p.m. interval for the operation of integrated samplers encompasses this large peak in traffic density. This fact, coupled with the very favorable patterns of wind direction and speed that occur from 3-7 p.m. (as discussed in the previous section), suggest that the afternoon sampling interval for integrated samplers should present the optimum conditions for assessing the freeway contribution of air pollutants. As expected, traffic density is lower and more uniform on Saturdays and Sundays.

CONTINUOUS POLLUTANT DATA

Carbon monoxide (CO) has been continuously monitored at the LACS sites by means of nondispersive infrared analyzers since June 1974. Chemiluminescence instruments for monitoring nitric oxide (NO) and nitrogen dioxide (NO_2) were added in January 1975 and instruments for ozone (O_3) added in January 1976. Flame photometric instruments for the determination of total gas phase sulfur (S) have been operated intermittently since May 1975. All continuous pollutant instruments are operated in pairs with one each at

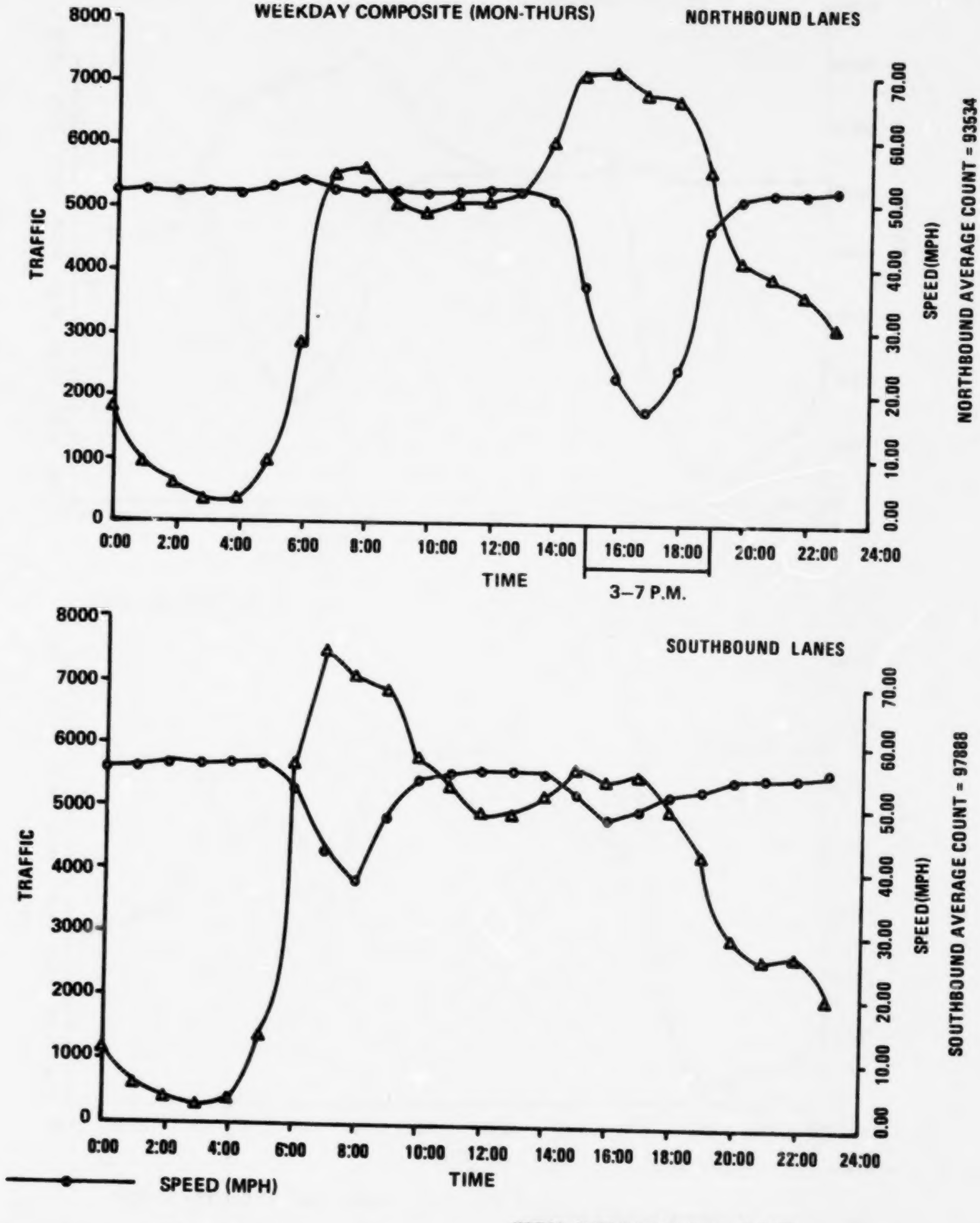

Figure 8. LACS traffic data.

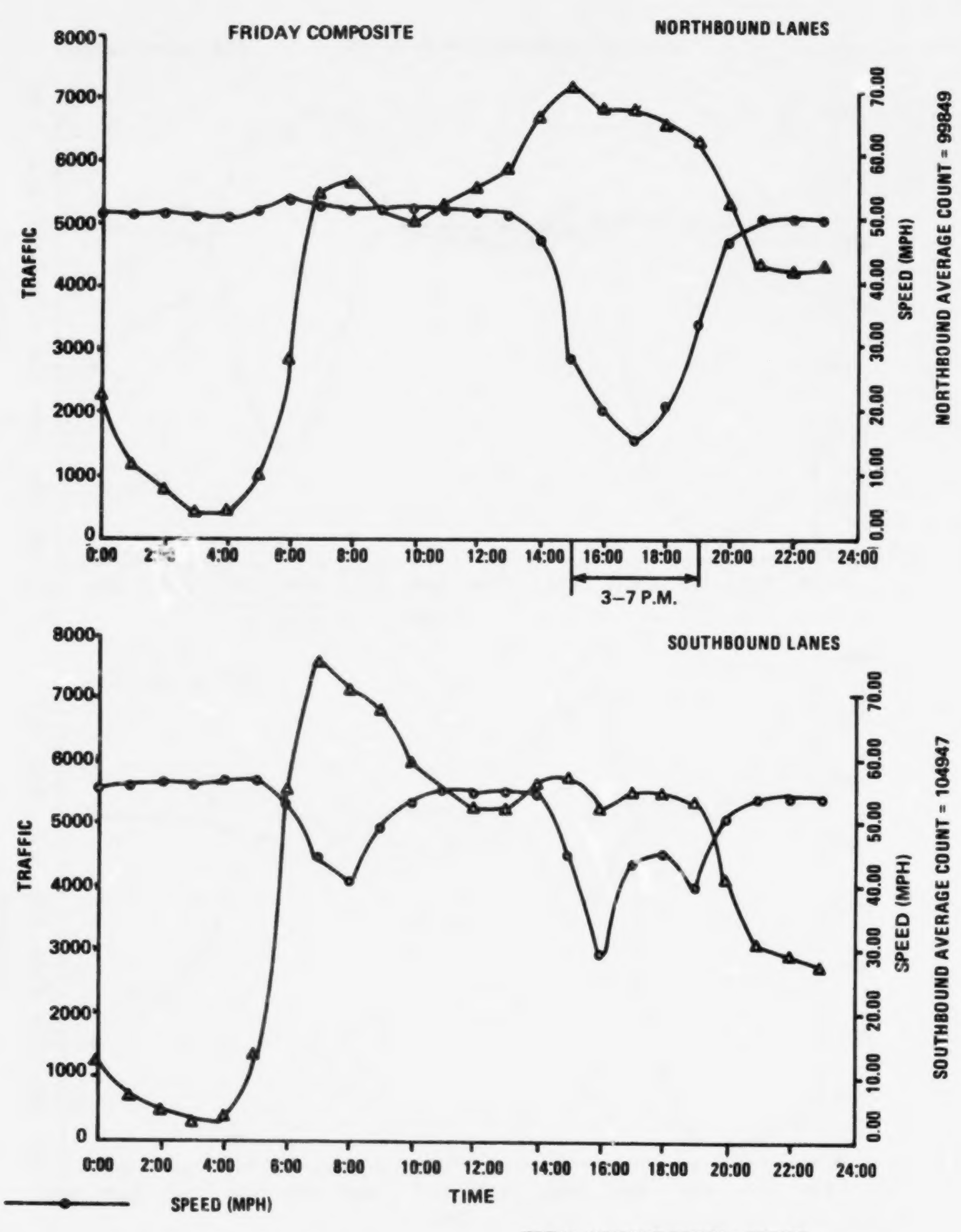

Figure 9. LACS traffic data.

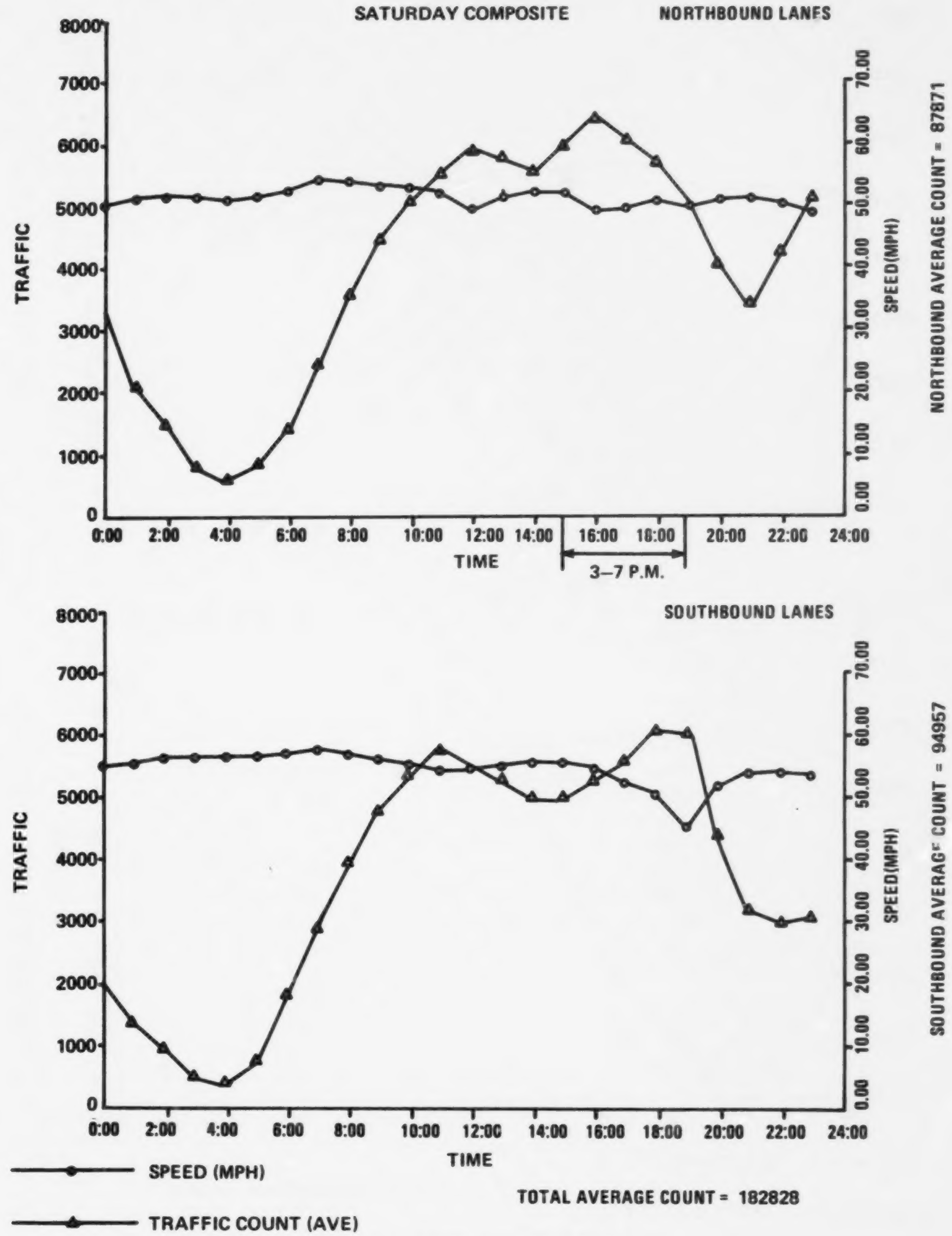

Figure 10. LACS traffic data.

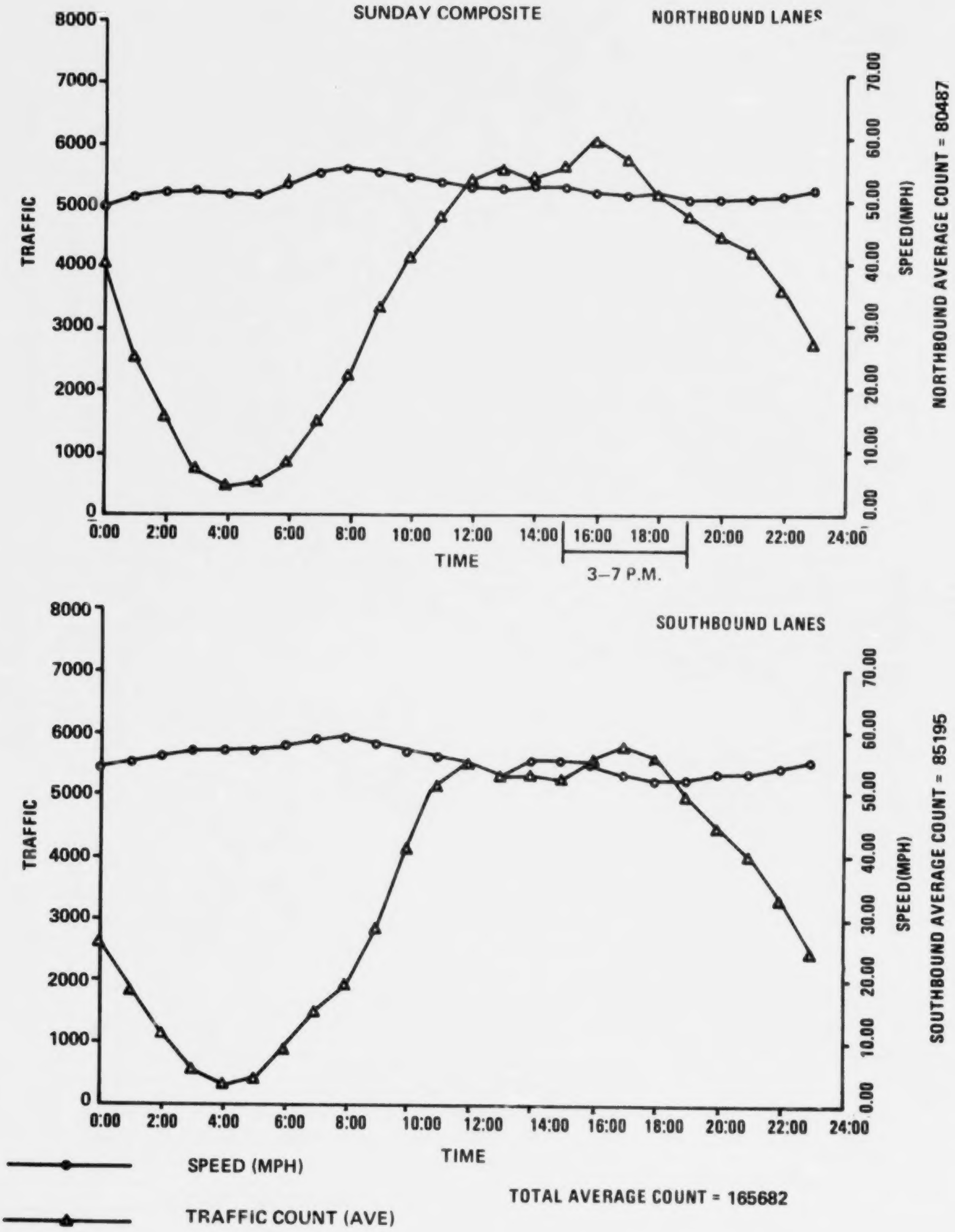

Figure 11. LACS traffic data.

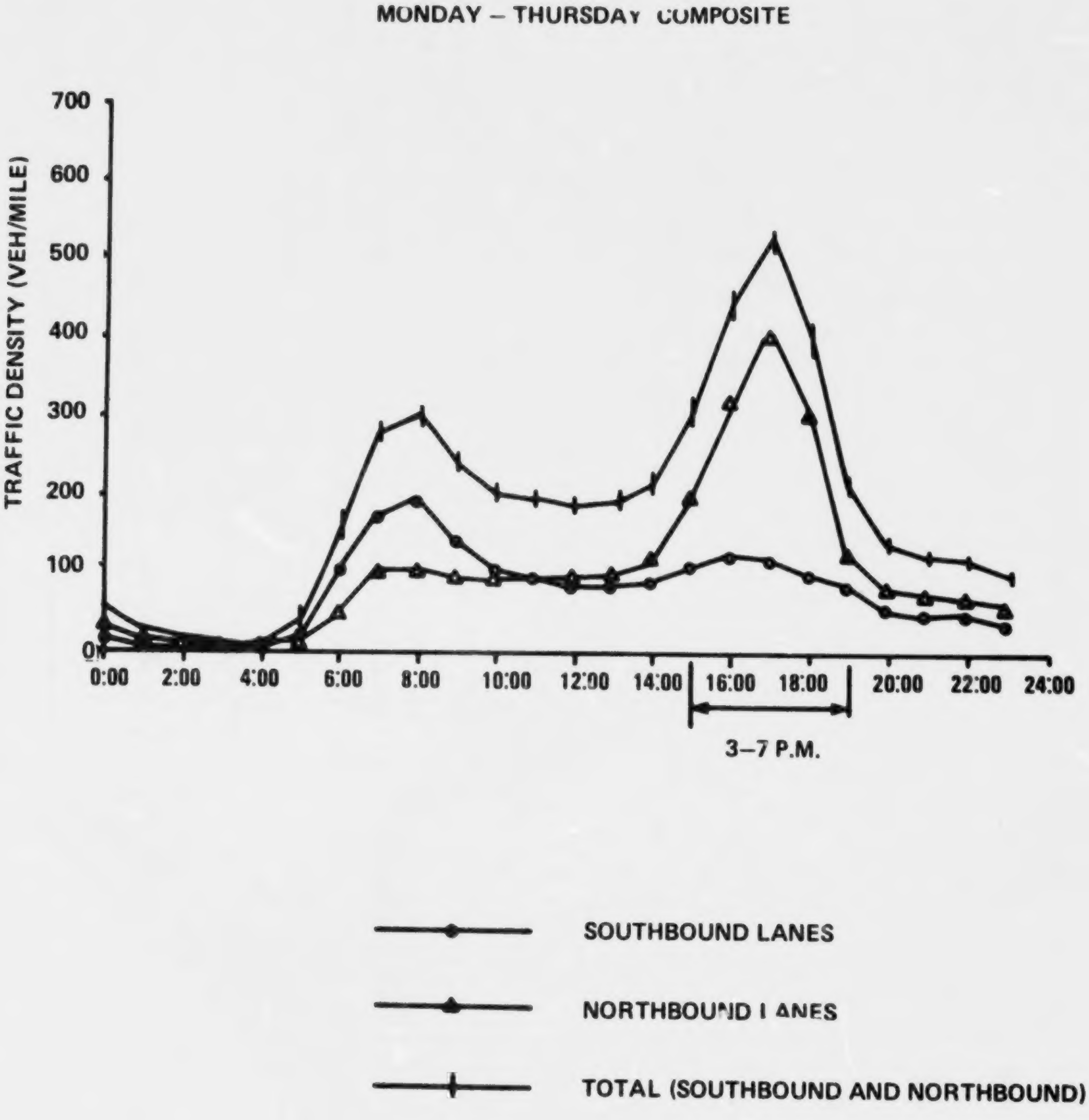

Figure 12. LACS traffic density (count/speed).

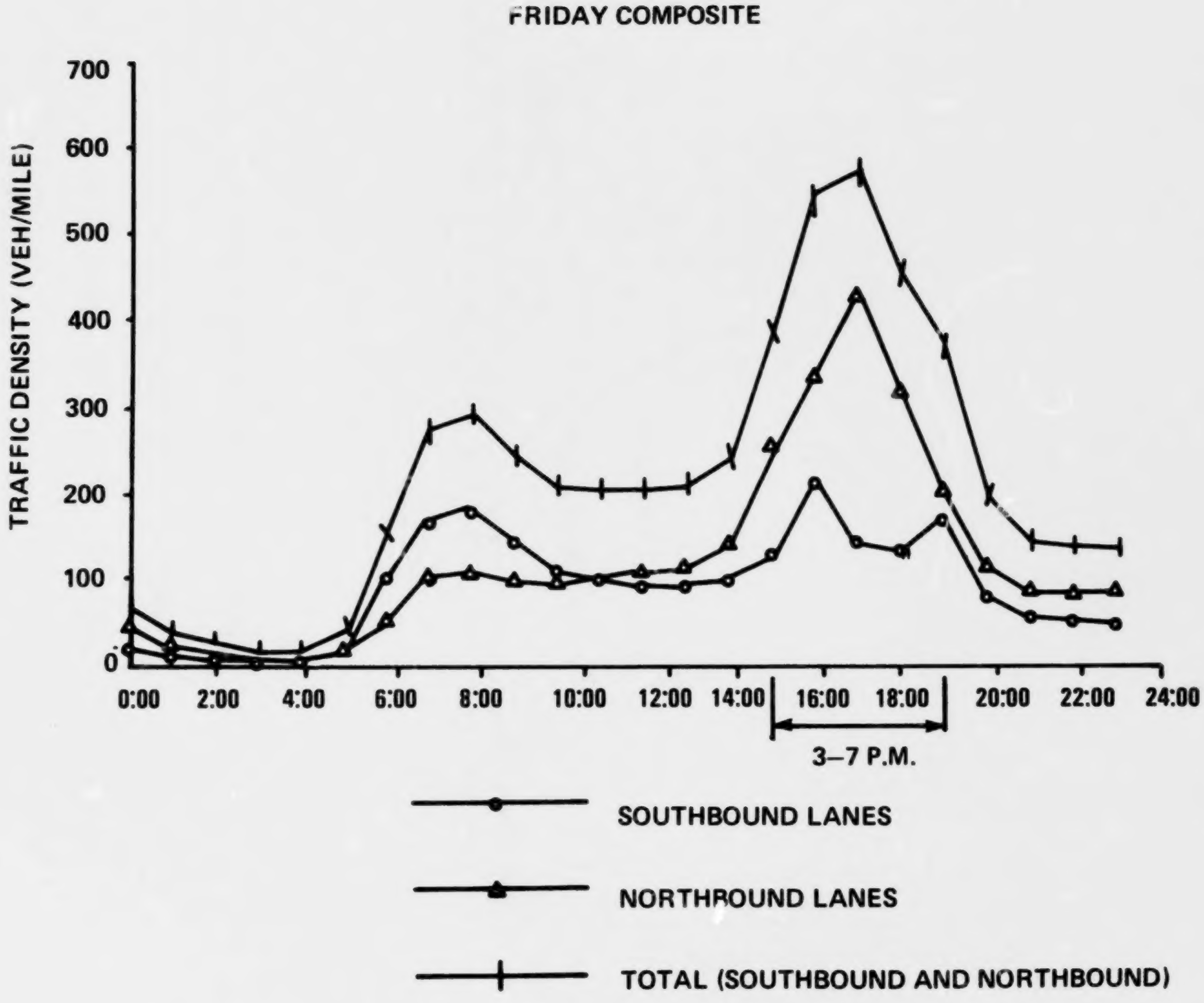

Figure 13. LACS traffic density (count/speed).

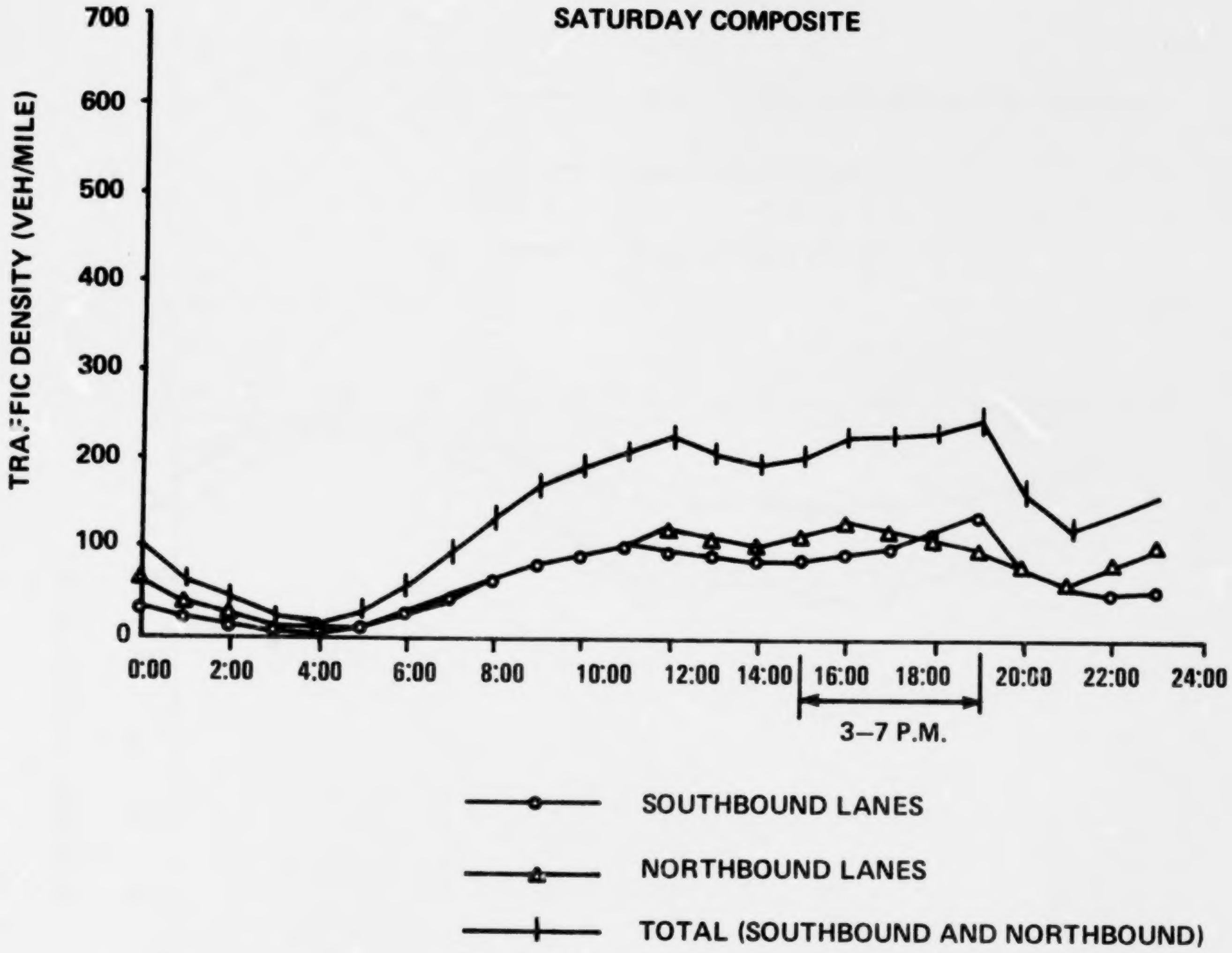

Figure 14. LACS traffic density (count/speed).

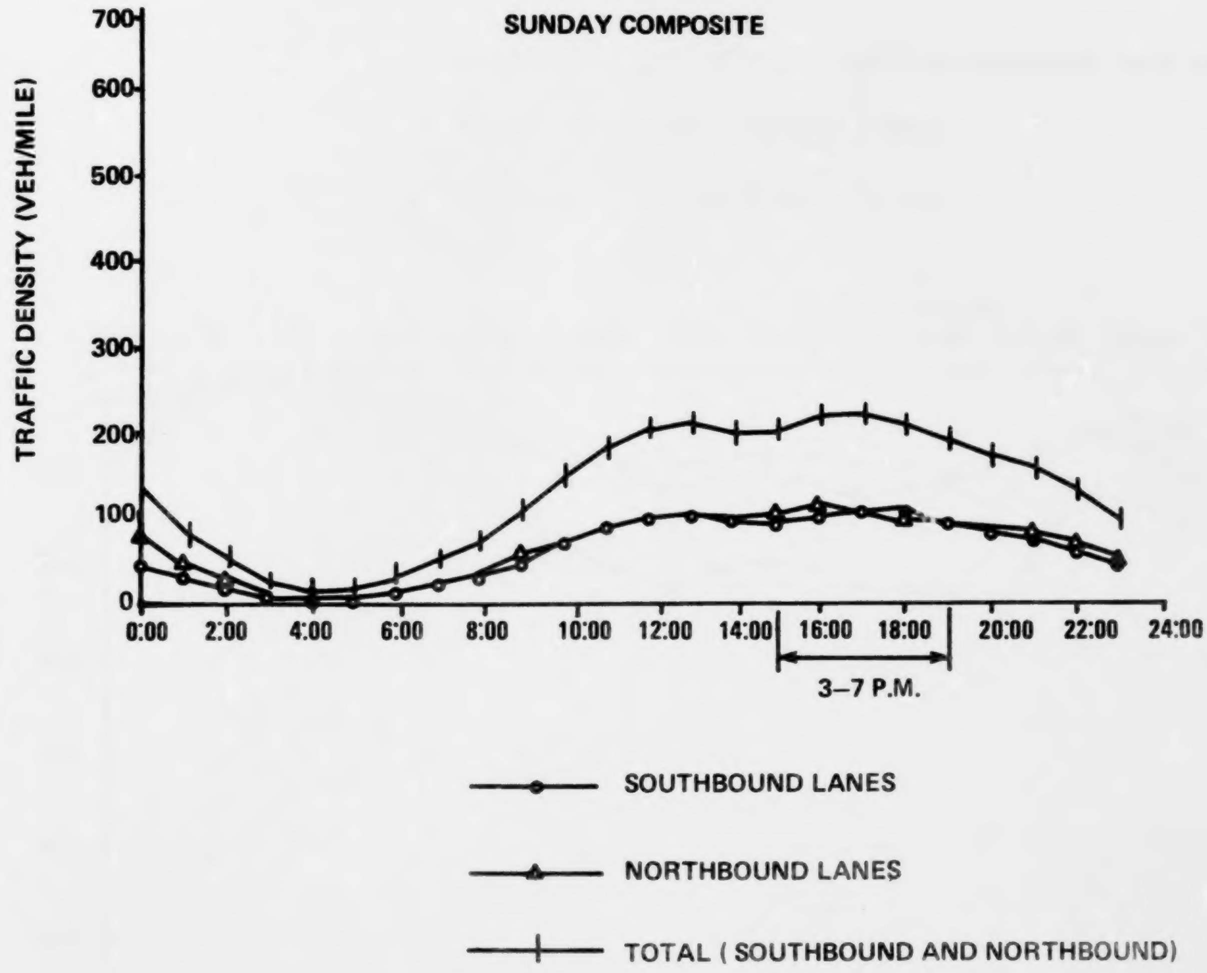

Figure 15. LACS traffic density (count/speed).

sites A and C. Inlet probes are at an elevation of about one meter above freeway grade (i.e., approximately at commuter elevation).

Figure 16 shows CO concentrations at site A, site C and the cross-freeway (C-A) difference as a function of wind direction. The plots were constructed using all valid CO data since the beginning of the study, stratifying by wind direction and computing average concentrations by site and for the average concentration difference (C-A) for each wind direction. It is interesting to note that when winds are calm (wind direction = 0), site C exceeds site A by about one part per million (1 ppm) due to a proximity effect (site C is 25 feet from the freeway while site A is 100 feet from the freeway). The cross-freeway difference (C-A) curve is slightly (<1 ppm) negative (A exceeding C) when winds are from the North, Northeast or East. It crosses the zero line when winds are along the freeway parallels (Southeast or Northwest) and is distinctly positive when winds are from the seabreeze mode (South, Southwest or West), reaching a maximum of about 5 ppm when winds are from the Southwest (i.e., perpendicular to the freeway). This pattern confirms the utility of the study design in making use of the naturally occurring seabreeze to separate emission products from background levels of automobile-generated pollutants.

In an attempt to investigate the effect of wind speed on pollutant concentrations, the CO data base was first sorted for all hours when the prevailing wind direction was from the Southwest (since these essentially perpendicular winds give rise to the largest cross-freeway differences). The restricted data base was then further stratified on the basis of wind speed intervals, and the average CO concentrations at site A, site C and the freeway difference (C-A) were computed for each interval. The results are plotted in Figure 17. Again, it is observed that site C substantially exceeds site A even at very light wind speeds due to the proximity effect. As wind speed picks up, the average CO concentration decreases at site A and increases at site C until wind speed reaches about 4.5 mph. Above this speed, the average CO concentration at both sites and the cross-freeway difference decrease due to the effect of increased dilution.

Figure 18 shows the diurnal pattern in CO concentration for each site and the cross-freeway difference as a composite of all summer months (April through September). The cross-freeway difference is very small during early morning hours but begins to build at about 7 a.m. as the seabreeze mode begins to predominate and the morning rush hour period begins. It levels off at about noon when the seabreeze mode is well established and the morning rush hour period subsides. Then at about 3 p.m. the cross-freeway difference increases again in response to the afternoon rush hour period, reaching a diurnal maximum of about 6 ppm at 5 p.m. Again, it is worth pointing out that the 3-7 p.m. sampling interval for integrated samplers appears to cover the optimum period for the detection of emission sources on the freeway.

Figure 19 shows the CO diurnal pattern as a composite of all winter months (October through March). Though similar in pattern to the summer months, the winter pattern is strongly affected by the shorter duration of the seabreeze mode. By 7 p.m., the cross-freeway difference in CO concentration has practically disappeared for the average winter day.

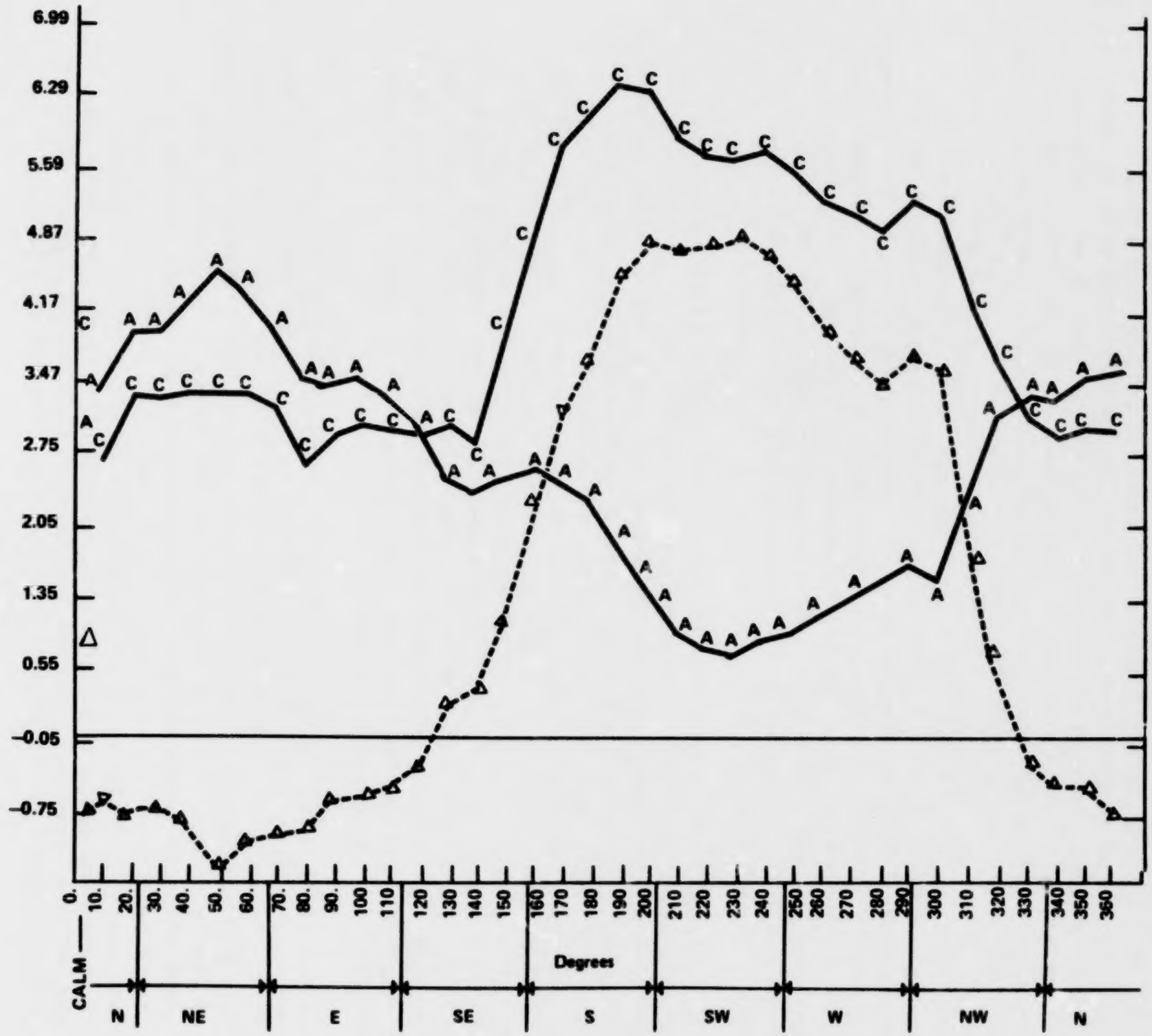

Figure 16. CO by wind direction (all data).

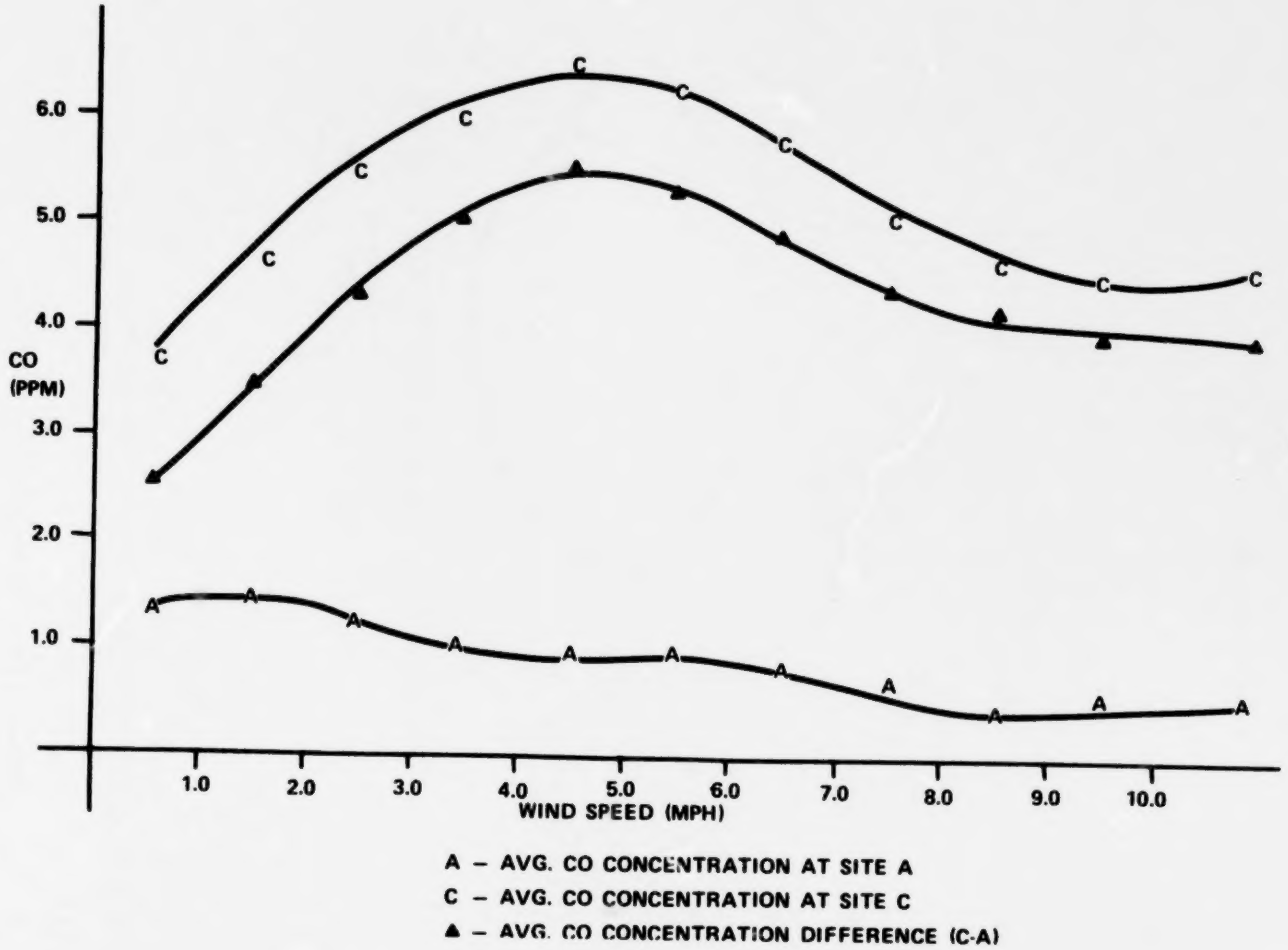

Figure 17. CO by wind speed for WD = SW.

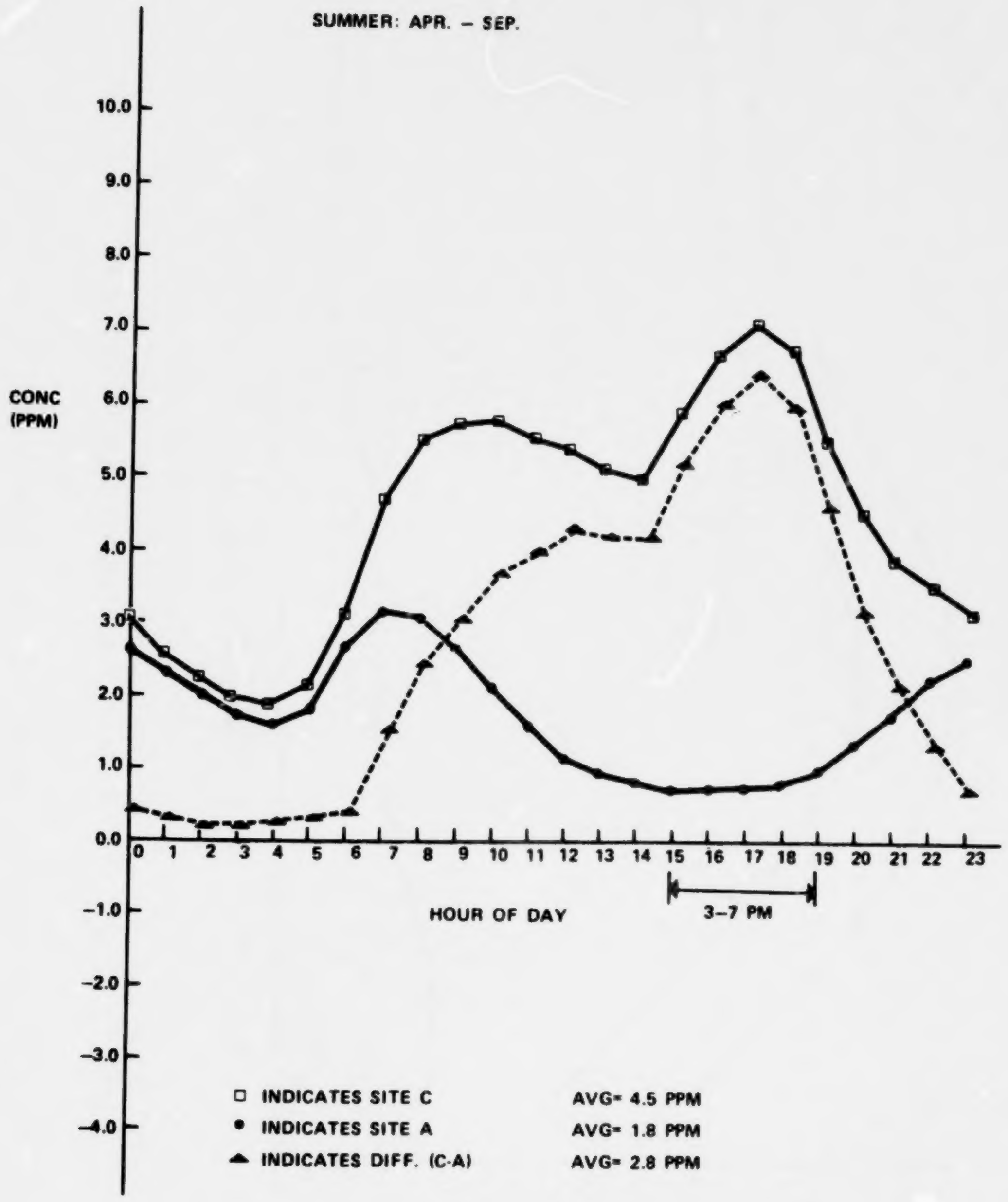

Figure 18. Carbon monoxide by hour.

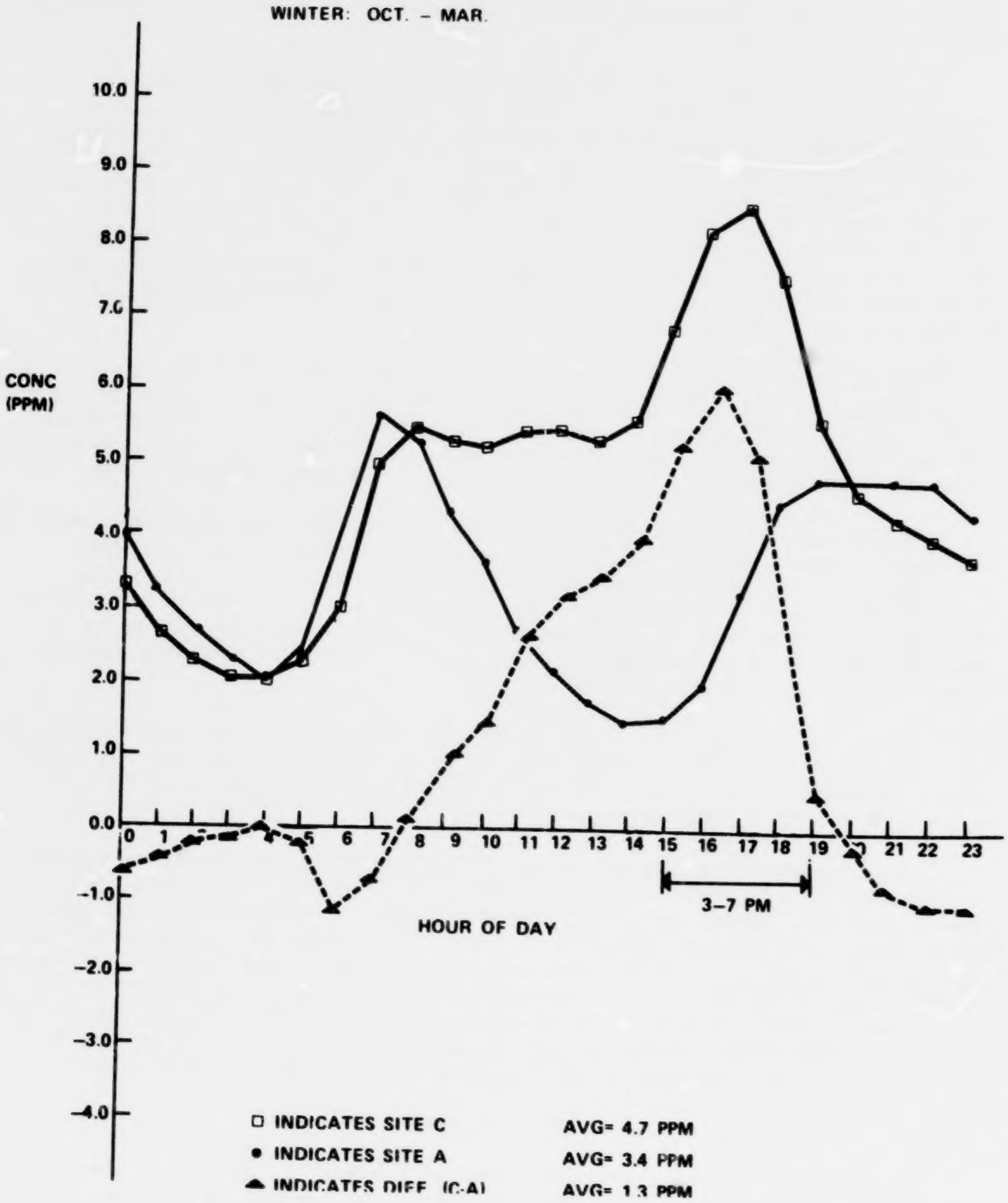

Figure 19. Carbon monoxide by hour.

The cross-freeway difference (C-A) in CO concentration is plotted again in Figure 20 to contrast the difference in diurnal pattern between weekdays (Monday through Friday) and weekends (Saturday and Sunday). The primary difference between the curves lies in the absence of an afternoon rush hour effect on weekend days.

As previously mentioned, an attempt was made to determine whether permanent LACS site A provided an adequate reflection of true background levels of automobile generated pollutants. To accomplish this, a temporary site (designated site A') was established in an open field at a distance of 700 feet from the freeway on the upwind side (see Figure 2). A CO analyzer was operated intermittently at site A' from June through September 1975. The diurnal patterns in CO concentration for site A, site A' and the difference (A-A') are plotted in Figure 21. Overall, the two sites agreed quite well throughout the course of the day and the apparent differences probably fall within the range of calibration error.

Nitric oxide is plotted as a function of wind direction in Figure 22. As with CO, the cross-freeway difference in NO concentration is maximized when winds are from the seabreeze mode (S+SW+W). Unlike CO, the NO concentration at site A practically vanishes under seabreeze conditions, suggesting that the background level of NO is very small in the Los Angeles basin.

Figure 23 is a similar plot for NO_2. Though not thought to be a primary pollutant, NO_2 is apparently formed in the traverse from site A to site C through a reaction with the NO emitted on the freeway and the O_3 in the background. The distinct peak in NO_2 concentration occurring at wind direction of 290° is thought to be related to a Southbound on-ramp which is oriented at that direction and feeds accelerating traffic onto the freeway just north of the sampling sites.

Ozone concentration as a function of wind direction appears in Figure 24. It appears that background ozone which is present during the daylight hours is essentially consumed in the traverse from site A to site C, giving rise to a negative difference curve.

In Figure 25, the summer season diurnal patterns for the cross-freeway differences (C-A) in the concentrations of NO, NO_2 and O_3 are plotted on the same graph. Emissions of NO become apparent at about 5 a.m. and the difference curve becomes positive at about 7 a.m. with the commencement of the seabreeze pattern. A positive cross-freeway difference in NO_2 concentration appears at about 9 a.m. coupled with a corresponding depletion of O_3 (negative cross-freeway difference). Apparently, there is not enough O_3 present in the freeway level background to completely react all of the NO emitted on the freeway within the traverse of air from site A to site C.

LONG TERM TRENDS

To evaluate trends in pollutant concentrations, it is first necessary to consider what changes may have occurred in the prevailing meteorological and traffic conditions at the LACS sites.

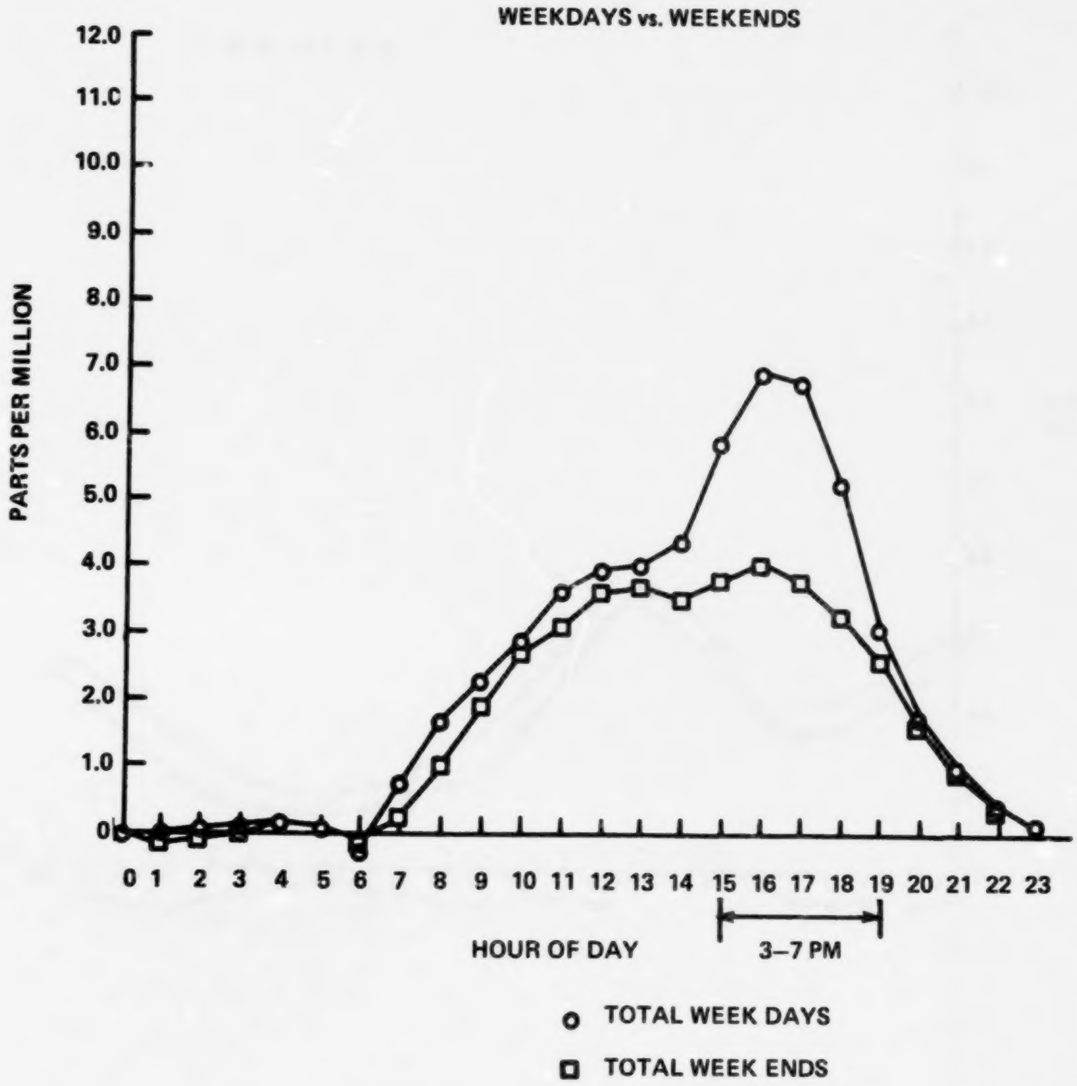

Figure 20. CO difference (C-A).

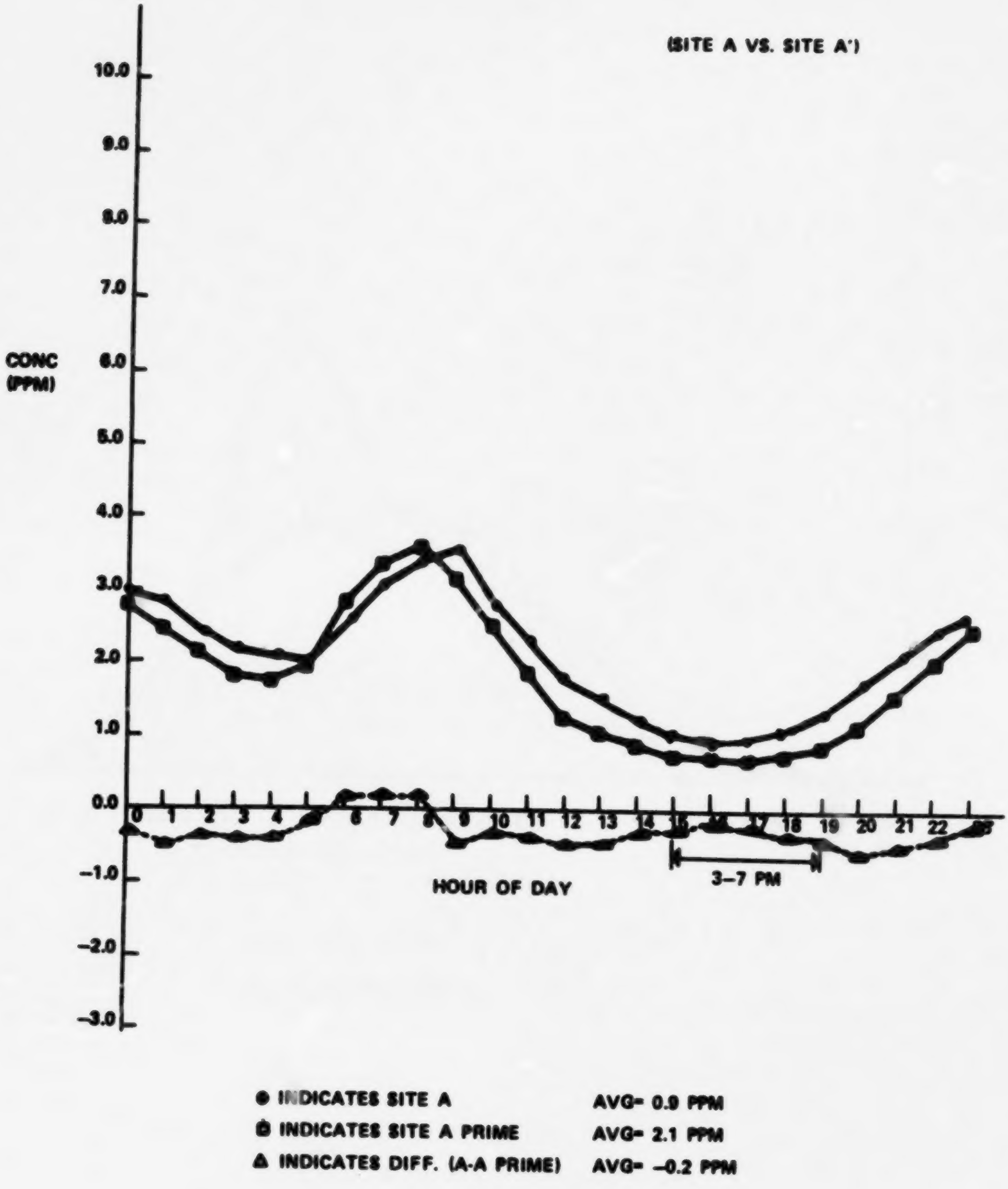

Figure 21. Background CO.

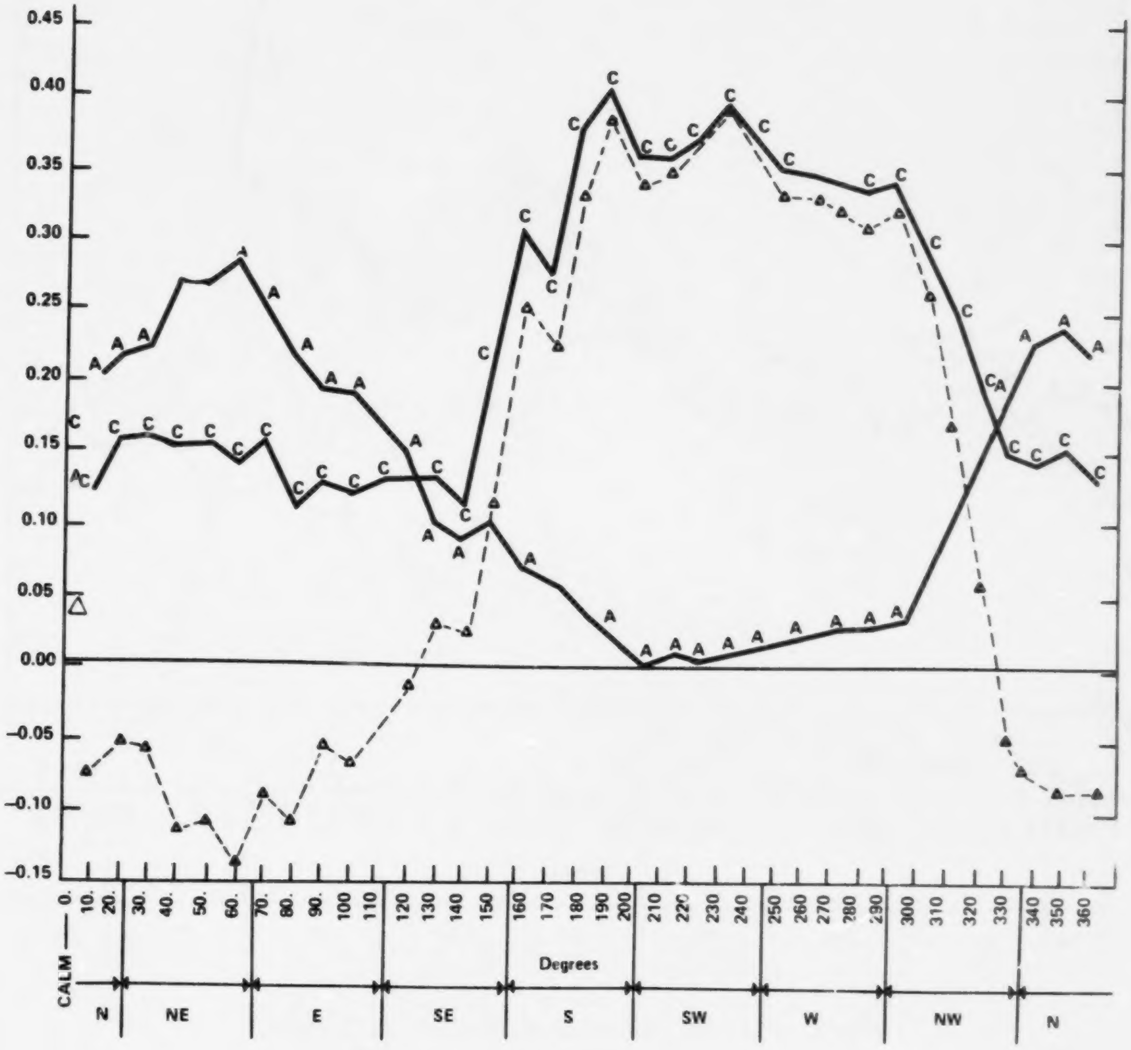

Figure 22. NO by wind direction (all data).

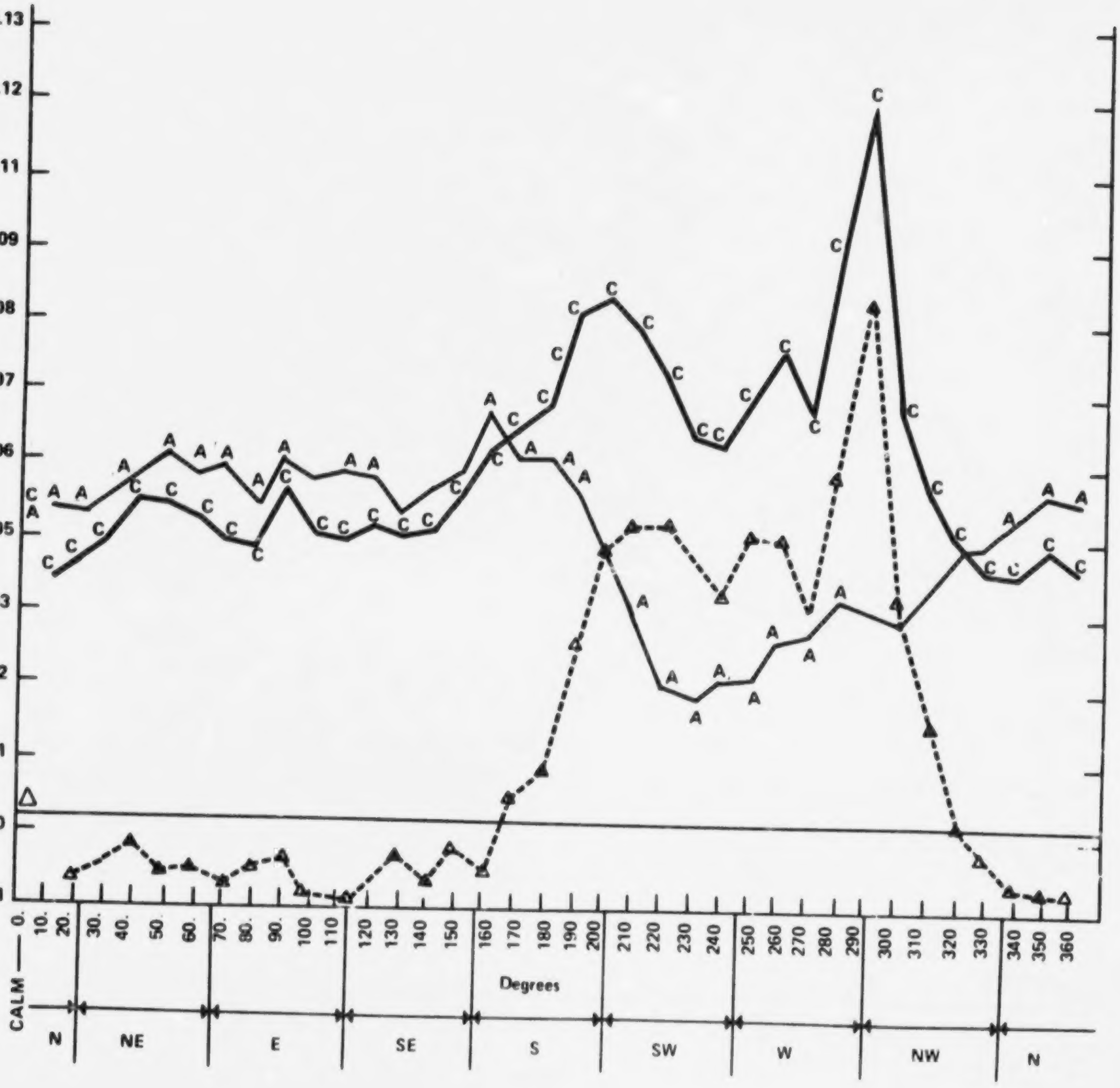

Figure 23. NO_2 by wind direction (all data).

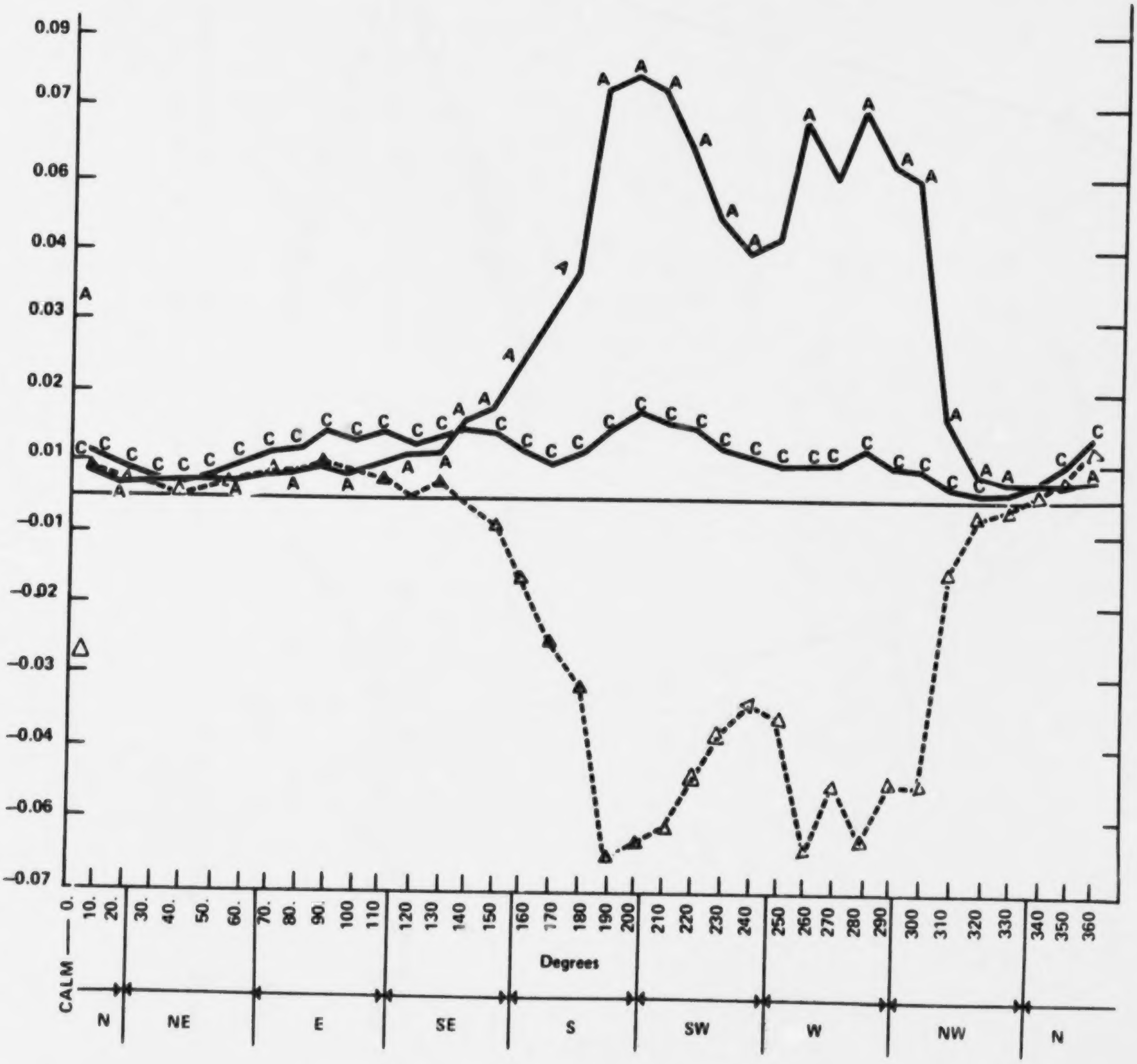

Figure 24. O_3 by wind direction (all data).

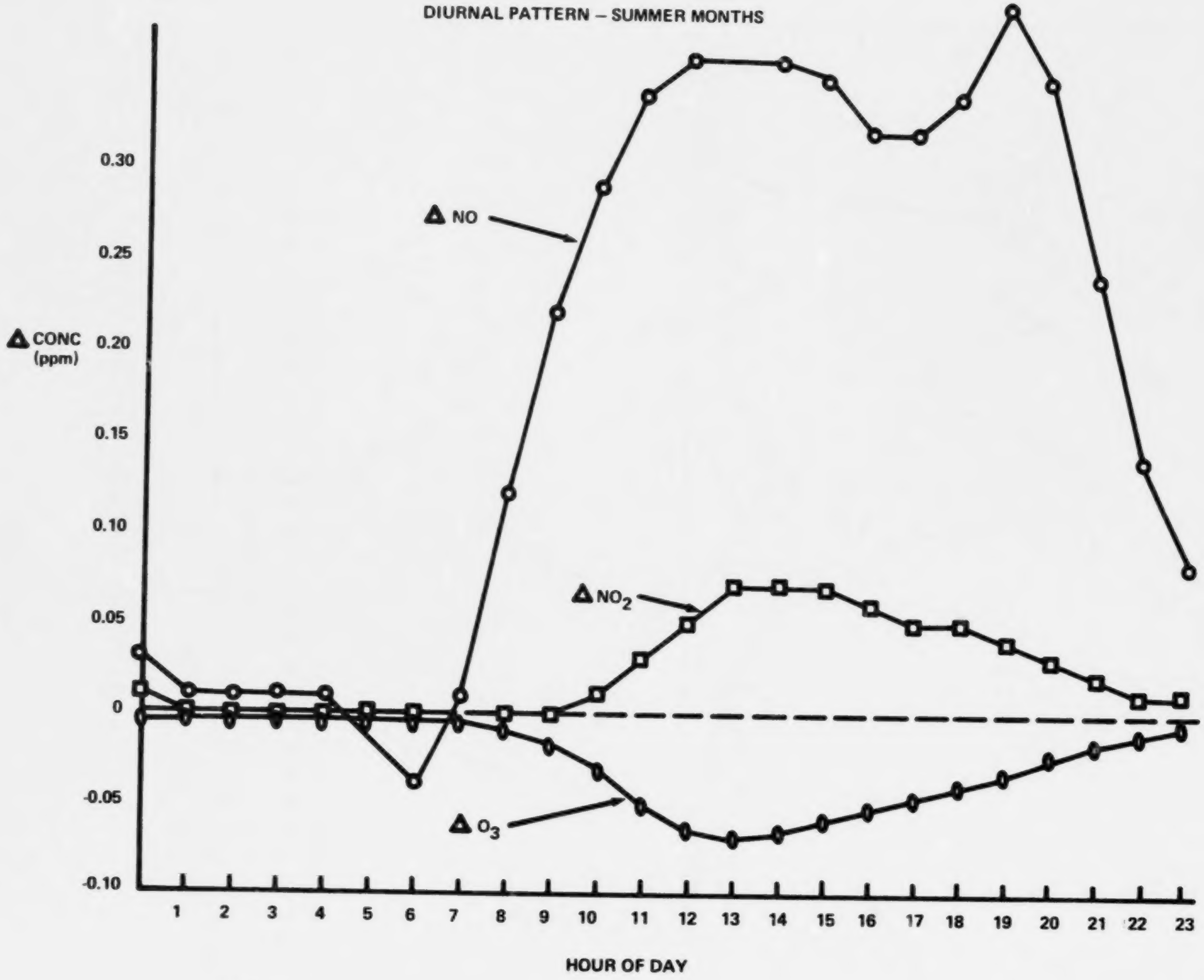

Figure 25. Cross-freeway differences (C-A) for NO, NO_2, and O_3.

Wind direction and wind speed data collected since the beginning of the study are summarized in Table II. The percent occurrence of favorable wind directions (i.e., seabreeze mode) and the accompanying average wind speed are presented separately for the two sample integrating time intervals employed in the study (i.e., 3-7 p.m. and 0-24 hours). The data are grouped chronologically on a seasonal basis (summer and winter) since this classification seems to provide reasonable intro-group homogeneity. The summer seasons, while certainly providing the best meteorological conditions for the monitoring program, exhibit a slight negative trend across the three years for both sampling intervals. The winter seasons show a great deal more variability, but, as pointed out in the footnotes, these seasons are not balanced in terms of data coverage and thus may not be directly comparable. The very unfavorable meteorology occurring in the winter of 1976, however, would be expected to have a notable impact on pollutant concentrations observed at that time.

As previously mentioned, on-site traffic count data are not available prior to September 1976. However, estimates of the annual average daily traffic volume at the LACS site for each of the last five years have been constructed through use of publications from the State of California Department of Transportation.[1] These data appear in Table III. With the exception of a slight decrease for 1974, the year of the gasoline shortage, traffic volume at this location along the San Diego Freeway has remained quite stable over the five year period.

In Figure 26, the trend in the percentage of Los Angeles County cars equipped with a catalytic converter is presented for two different methods of estimation. The lower curve was generated by Rockwell Air Monitoring Center (RAMC)[2] from county sales registration data, while the upper curve was generated by TRW, Inc.[3] by adjusting the Rockwell estimates for actual vehicle miles travelled as a function of model year. This latter curve is considered more representative of the real vehicle mix on the San Diego Freeway. It indicates that catalyst equipped vehicles accounted for approximately 30% of the vehicle miles travelled in the Los Angeles basin as of December 1976.

Figures 27-29 are bar graphs showing the seasonal averages at each site and for the cross-freeway difference (C-A) in the concentrations of CO, NO and NO_2. As previously discussed, the summer season data (shaded bars) provide the best opportunity to assess long-term trends.

As shown in Figure 27, there has been no discernible change in the background (site A) concentration of CO since the beginning of the study. The freeway contribution of CO (C-A), however, increased slightly from the summer of 1974 to the summer of 1975 (possibly in response to the increase in total traffic volume) and then decreased by about 25% from summer of 1975 to the summer of 1976. This substantial decrease must be attributed to the phase-in of catalyst equipped vehicles.

Figure 28 shows very little change in the background level, but a substantial increase in the freeway contribution of NO between the summers of 1975 and 1976. Similarly, NO_2 (Figure 29) has exhibited a constant background

TABLE II. AVERAGE % FREQUENCY FROM S+SW+W AND THE ASSOCIATED AVERAGE SPEED BY SEASON AND SAMPLING INTERVAL

Season[a]	Sampling Interval			
	15-19 hr.		0-24 hr.	
	% WD (S+SW+W)	Avg. WS, mph	% WD (S+SW+W)	Avg. WS, mph
Summer, 1974[b]	93.3	5.6	63.6	3.5
Winter, 1974	69.7	4.5	34.9	3.7
Summer, 1975	97.2	6.0	62.3	3.6
Winter, 1975[c]	78.3	4.5	39.5	3.8
Summer, 1976	95.9	5.7	58.9	3.5
Winter, 1976[b]	37.0	3.2	28.1	3.0
Overall Summer	97.0	5.8	61.3	3.5
Overall Winter	64.8	4.2	34.8	3.6

[a] Summer - April thru September
Winter - October thru March

[b] Season began June 1, 1974

[c] No data available for December 1975 or January 1976

[d] Season ended December 15, 1976

TABLE III. SAN DIEGO FREEWAY TRAFFIC VOLUME @ LACS SITE FIVE YEAR HISTORY

Year	Average Daily Total	Percent Change
1972	181,500	
1973	182,500	+ 0.6%
1974	180,000	- 1.4%
1975	182,500	+ 1.4%
1976	183,000	+ 0.3%

Source: State of California Department of Transportation (estimates)

Note: LACS Avg. Daily Total (Sept. - Dec. 1976) = 188,457

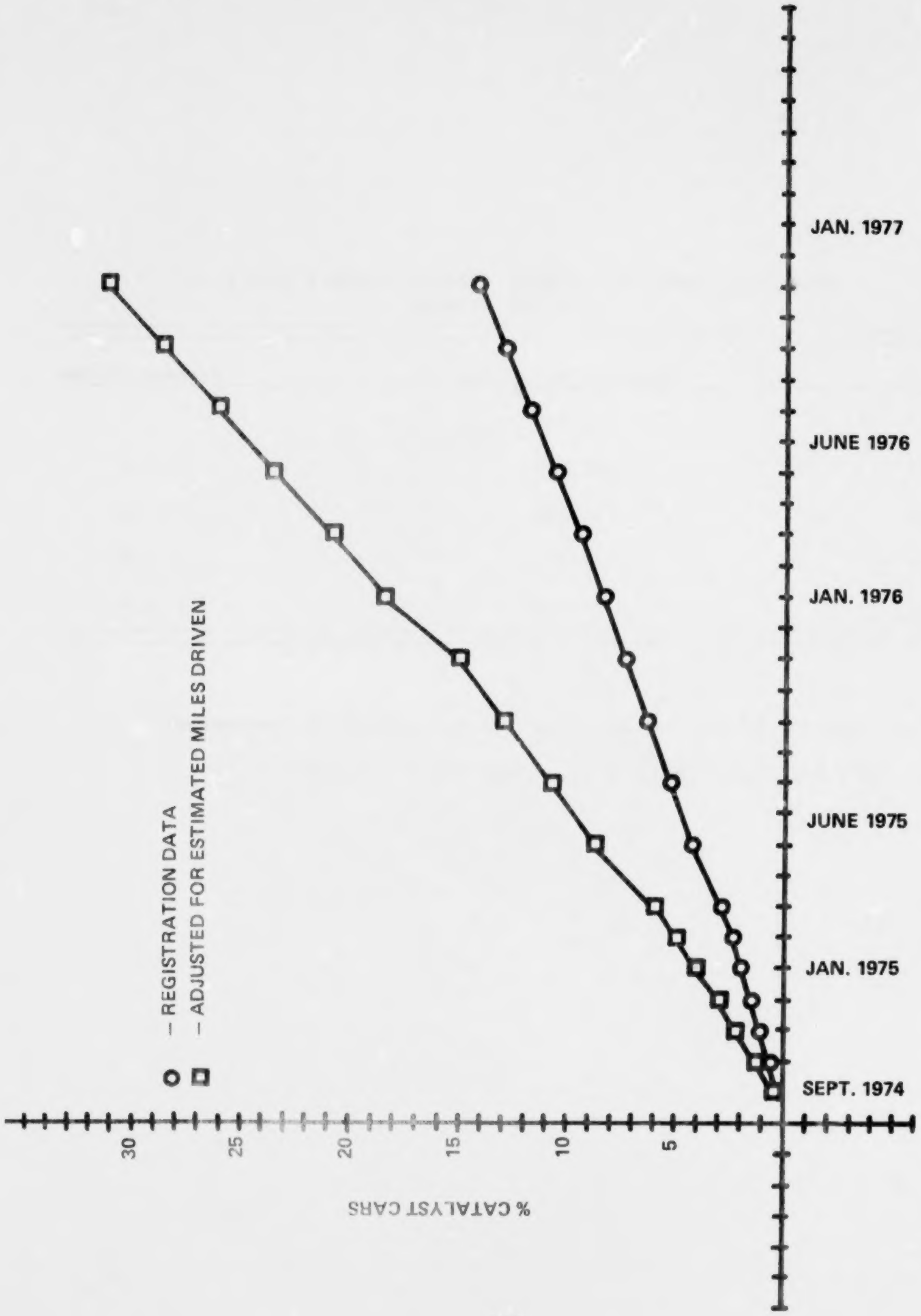

Figure 26. Percent catalyst cars - LA County.

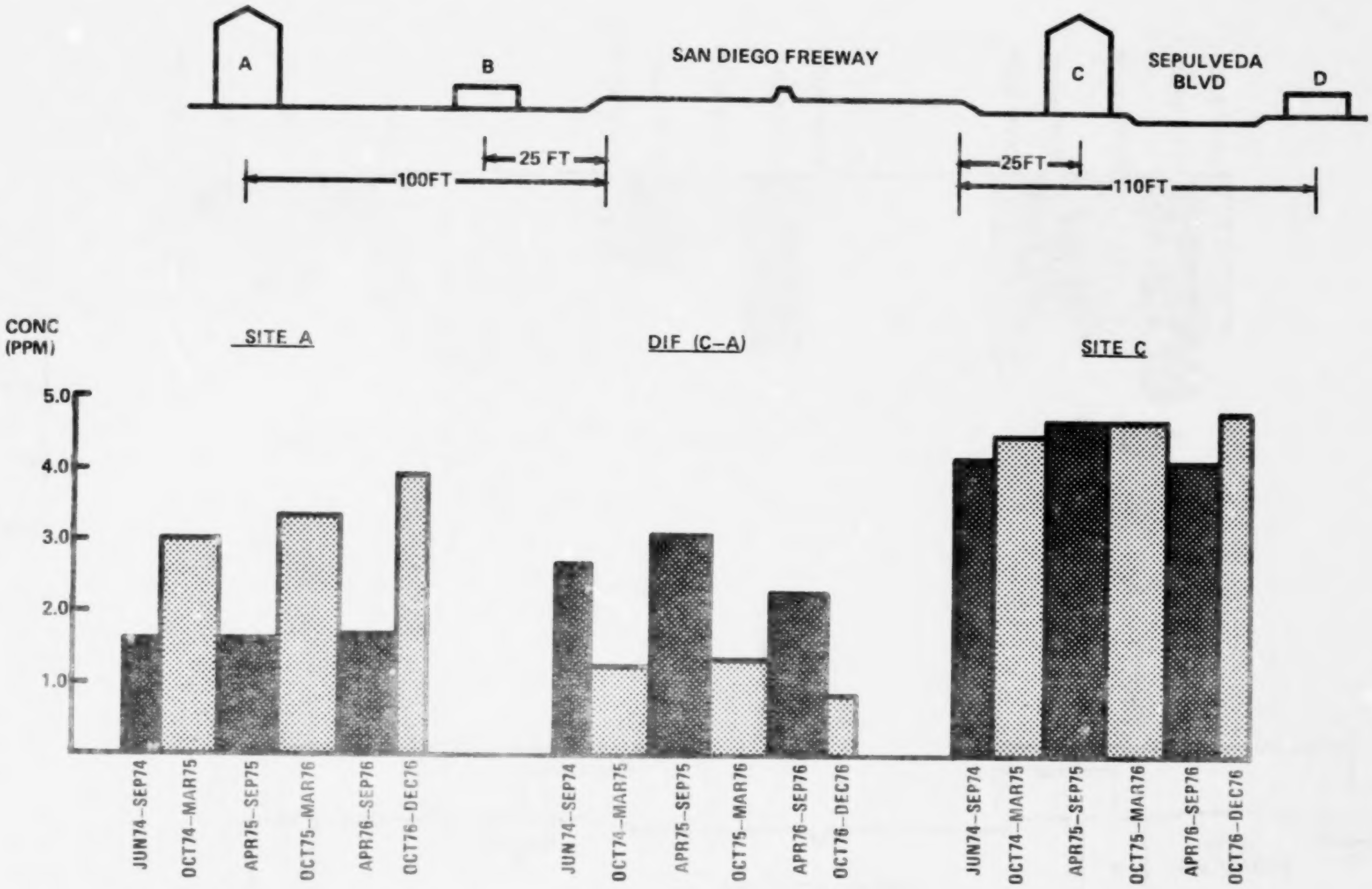

Figure 27. CO - average concentrations by season.

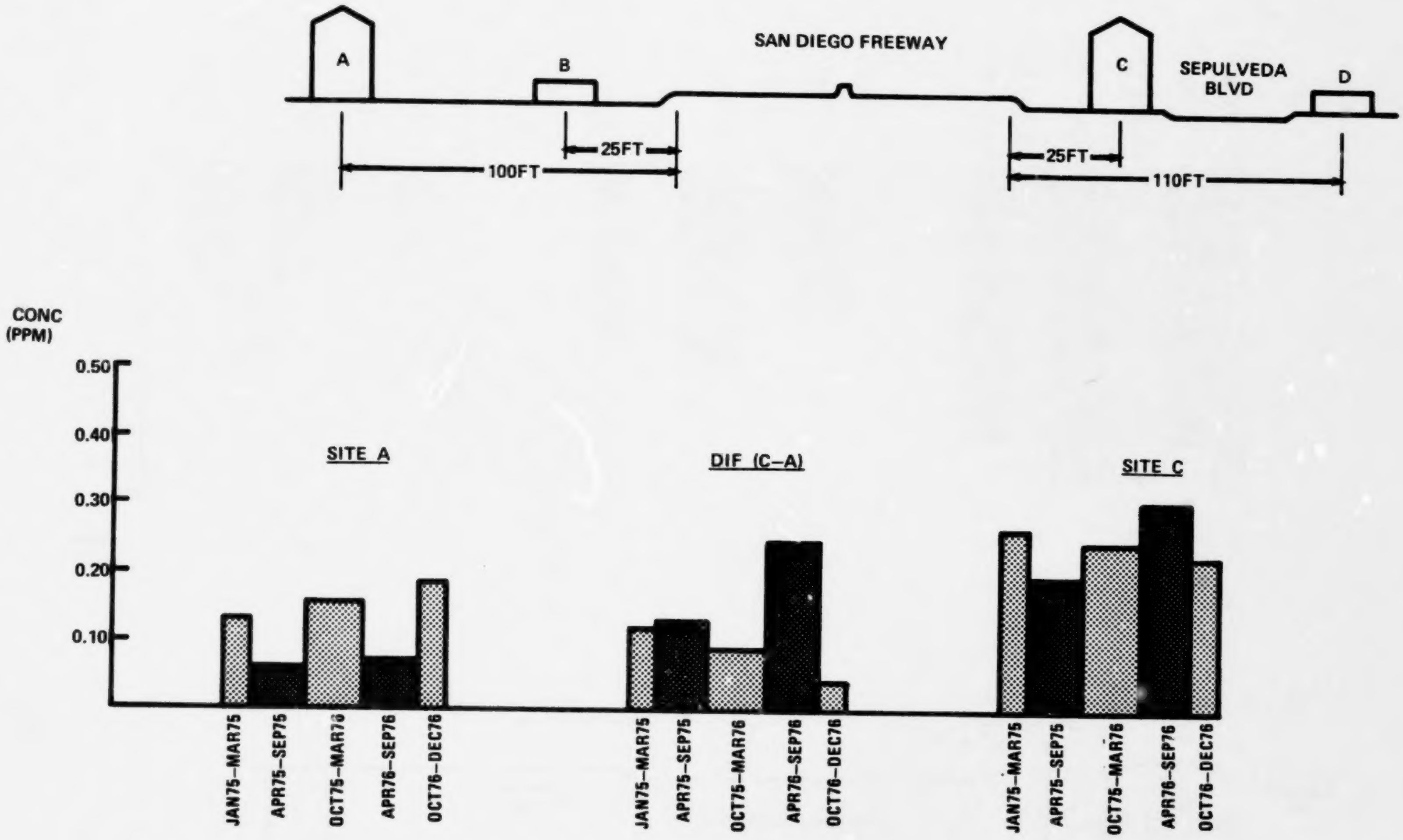

Figure 28. NO - average concentrations by season.

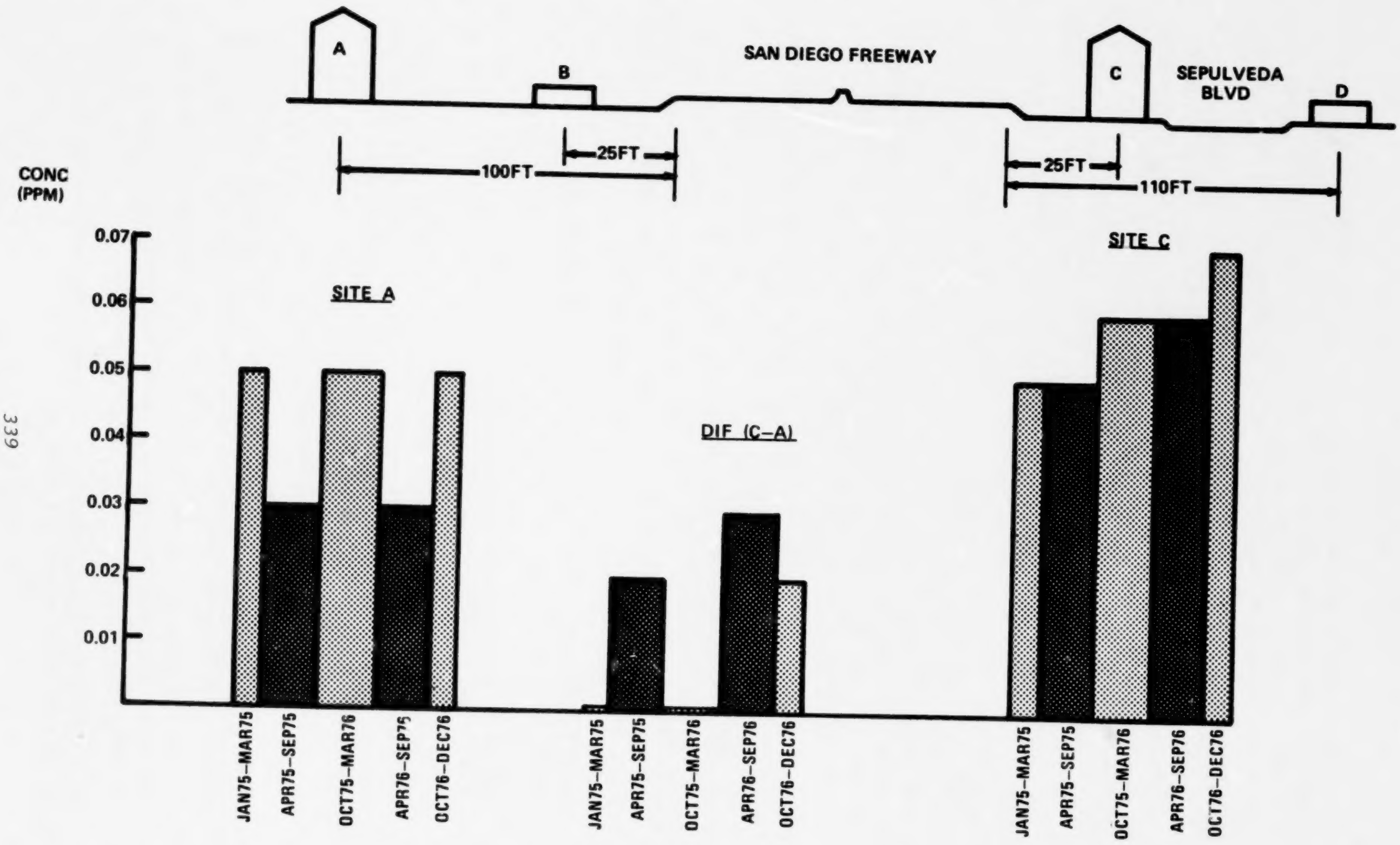

Figure 29. NO_2 - average concentrations by season.

level and a large increase in the freeway contribution. With only two summer seasons to compare, it is not realistic at this time to attribute these increases to the function of the catalyst. Ozone data are available only for 1976 and, thus, inferences about trends cannot be drawn at this time.

Figure 30 consists of plots of the monthly average cross-freeway differences (C-A) in the concentration of all continuously monitored pollutants. The monthly average percent occurrence of favorable wind directions is plotted at the bottom of the figure for comparison. It is interesting to note how closely the cross-freeway difference in CO concentration follows the wind direction pattern. Sulfur dioxide (SO_2) bubbler data is shown in the figure for comparison with total sulfur. Because of the very low SO_2 levels involved, the data from the total sulfur analyzers is considered somewhat questionable.

CONCLUSIONS

- The LACS site appears to be a very favorable location in terms of meteorology and traffic flow for determining the freeway contribution to ambient concentrations of air pollutants. This is especially so during summer months and between the hours of 3-7 p.m.

- Traffic volume estimates from the California Department of Transportation in conjunction with on-site traffic data indicate that there has been little change in the traffic flow on the San Diego Freeway at the study site from 1974 through 1976. The diurnal patterns in traffic count and speed by day of week are very consistent from week to week. As of December 1976, the total traffic volume passing the study site averaged 188,000 vehicles per day with an estimated 30% of the vehicle miles travelled attributed to catalyst equipped vehicles.

- The background levels of CO, NO and NO_2 have remained essentially constant since 1974.

- The freeway contribution of CO decreased about 25% from 1975 to 1976 while the freeway contribution of NO and NO_2 increased substantially.

- There is apparently an inadequate amount of background O_3 at freeway level to convert all of the emitted NO to NO_2. The reaction of NO with O_3 proceeds rapidly enough so that near zero concentrations of O_3 are observed at the near downwind site.

REFERENCES

1. State of California, Department of Transportation, Traffic Volumes on California State Highways: 1972, 1973, 1974, 1975 and 1976 (perprint).

2. Rockwell Air Monitoring Center, "Determination of Percentage of Diesel Trucks and Catalyst Equipped Cars," Proceedings of the LACS Symposium, April 12 and 13, 1977.

3. TRW, Inc., "A Mobile Source Emission Inventory System for light Duty Vehicles in the South Coast Air Basin."

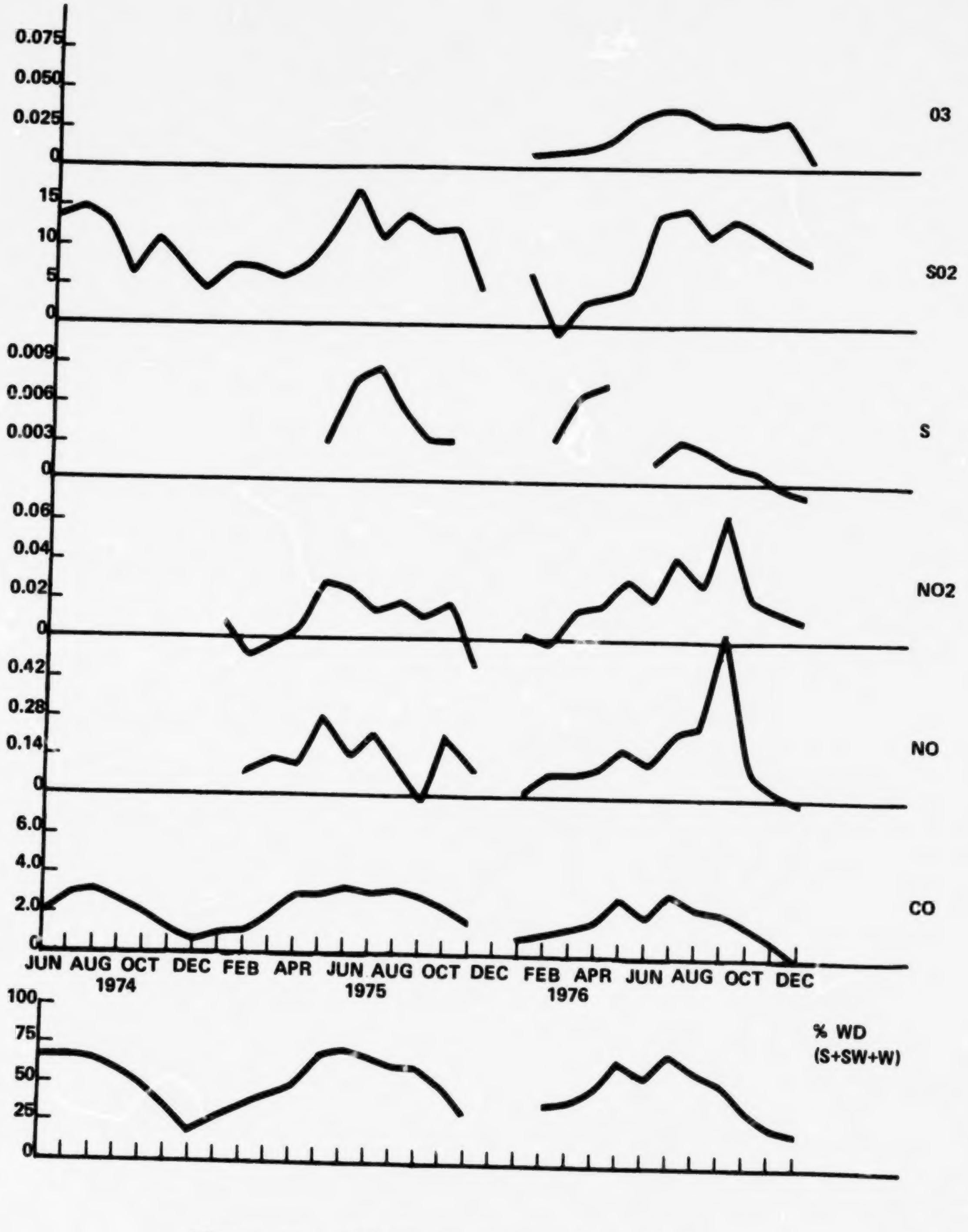

Figure 30. Difference C-A for hours 0-24.

NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE INTERRELATIONSHIPS ACROSS THE FREEWAY

Robert K. Fankhauser

Environmental Protection Agency
Research Triangle Park, North Carolina

on assignment from the

National Oceanic and Atmospheric Administration
Silver Springs, Maryland

ABSTRACT

The Los Angeles Catalyst Study has produced a combination of basic data that are available over a period of several years. Among the data are measurement of wind, traffic count with traffic speed, ozone, nitric oxide, nitrogen dioxide, carbon monoxide, and particulate. Many data are available at sites of the Freeway. This brief study relates nitric oxide, nitrogen dioxide, and ozone with wind and traffic. All data are not concurrent since one or another instrument has been added or taken out of service, but significant data exist. Certain data verify chamber studies. Plots of simultaneous values of the hourly measurements show that changes occur as air acquires pollutants in passing across the Freeway.

The Los Angeles Catalyst Study (LACS) is producing a unique set of data because of its location, the completeness of the instrumentation and the duration of operation. Its design is to sample emmisions from heavy traffic. Its location is such that meteorological conditions are unusually repetitive. Its operation has been for an unusually long period compared to other air pollution studies.

For this microstudy, data for periods in May and September 1976 were plotted along with wind speed and direction. Traffic data were available beginning with September. For sites A and C the data included hourly values of ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2) as well as wind speed and direction. The wind equipment was located at site A.

These sites are on opposite sides of the San Diego Freeway with the Freeway running from approximately SSE to NNW (145° - 325°) at a point about 0.5 mile north of the Wilshire Boulevard interchange, which is about 6.4 km (4 miles) from the ocean. The ocean-to-land breeze is established fairly early in the day (around 0900) during May through September and continues until 1800-2100. Wind speeds during the daytime seldom are over 3 meters per second (mps) or 7 miles per hour (mph) for an hourly average. During the night when

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the ocean-to-land breeze has subsided, the average hourly speed is usually less than 1 mps (2-3 mph). At these lighter speeds the direction is not as constant so that even though the prevailing wind for an hour is judged to be, as an example, from the N there are usually excursions from the direction to either side and even to the exact opposite direction. Thus during any one hour the opposing sites may share the emissions from the Freeway rather than receiving them exclusively. The lighter wind speeds would also not disperse the emissions as rapidly.

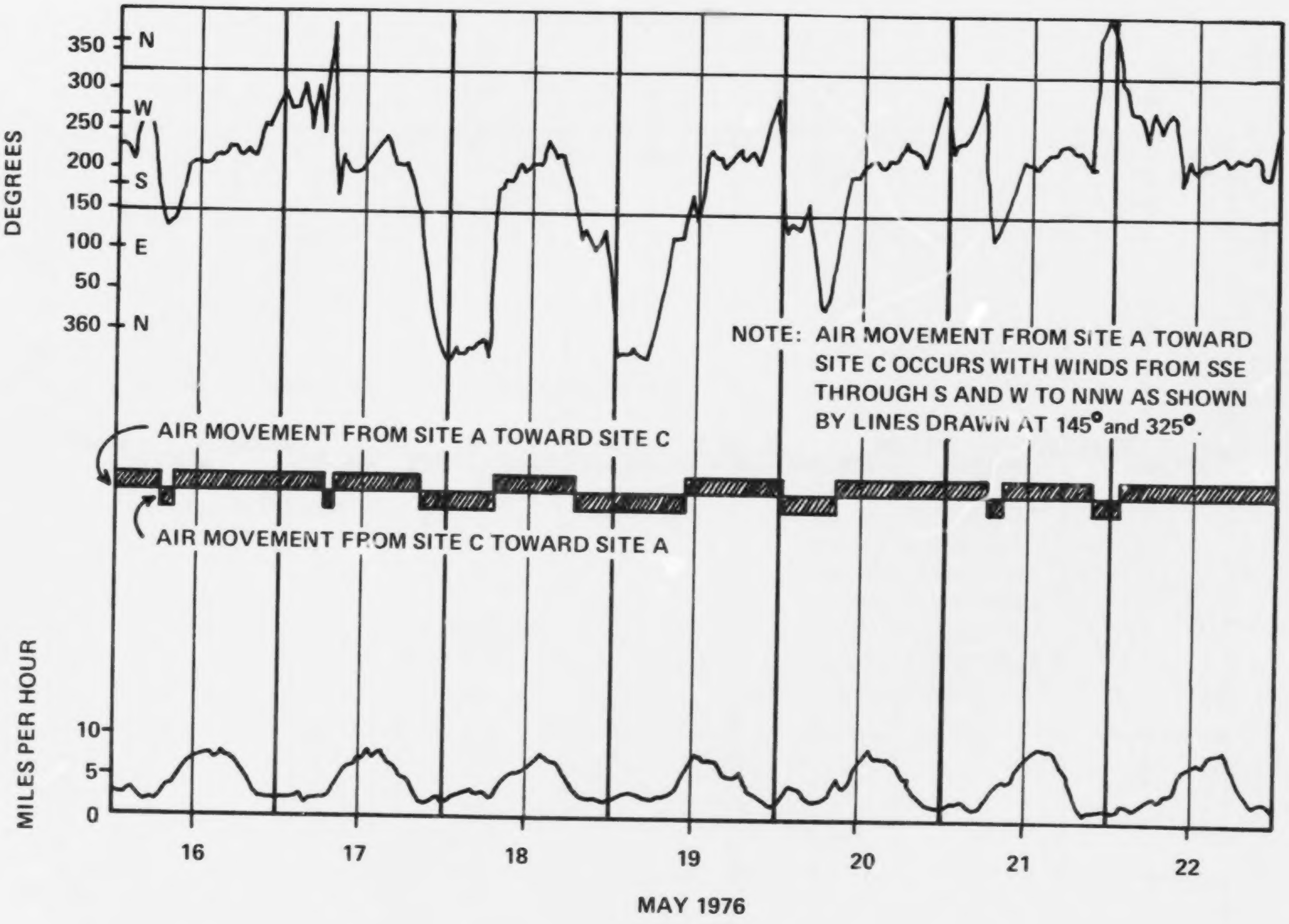
A large part of the differences in patterns of the pollutant concentrations that are seen between site A and site C is due to the different distances from the traffic. Site C is a little less than 8 m (25 ft.) from the northbound side of the San Diego Freeway. Sepulveda Boulevard is about the same distance on the other side of site C so traffic on it (small compared to Freeway traffic) also contributes pollution. Site A is about 30 m (100 ft.) away from the southbound edge of the San Diego Freeway (on the side towards the ocean). Site C is within the path of the turbulent eddies produced by fast moving northbound traffic while at site A such eddies have become indistinguishable from the general air flow. Of course the distant edge of the southbound lanes is farther from site C than it is from site A. The general effect is that at site A with winds that have a component moving air from A toward C there is little or no pollution from the Freeway. At C however the Freeway is always a contributor and there is also a small contribution from Sepulveda Boulevard with wind in the C to A direction.

It must be remembered that the sites are surrounded by metropolitan Los Angeles which supplies a background concentration of these same pollutants. The background concentration rises and falls hourly in somewhat the same pattern as that due to the Freeway since other activity in the city is geared to the same phenomena which cause the Freeway traffic to change.

The first graphs of data (Figures 1 and 2) are of the wind directions and speeds for a period in May and another in September. Since the Freeway at this point lies along the line of approximately 145^{o} to 325^{o} (SSE to NNW) these directions have been drawn in to show which winds carry air from site A towards site C and vice versa. Winds vary direction so continuously that for directions nearly parallel to the Freeway, sites on both sides of the Freeway are likely to receive some pollution during such a period.

To show the times when the wind has a component from C to A or from A to C, a bar graph was drawn in the center of Figures 1 and 2. This portion of Figures 1 and 2 will be used in other figures to show more simply the effect of direction on concentrations of pollutants related to Freeway traffic.

At site A (see Figures 3 and 4) during the time of the ocean-to-land breeze (air movement from site A toward site C) the concentration of O_3 rises to a peak usually between 1200 and 1500. The concentration pattern follows relatively closely the pattern of wind speed and insolation. The wind speed is likely to be related to the mixing height. That is, as the sun's heat produces rising and falling columns of air the stagnant layer at the surface is "geared in" with the faster moving air aloft and so is carried along at an increased speed. Air from a layer above the surface is mixed downward so pa



AIR MOVEMENT FROM SITE A TOWARD SITE C

AIR MOVEMENT FROM SITE C TOWARD SITE A

NOTE: AIR MOVEMENT FROM SITE A TOWARD SITE C OCCURS WITH WINDS FROM SSE THROUGH S AND W TO NNW AS SHOWN BY LINES DRAWN AT 145° and 325°.

Figure 1. Wind data - Los Angeles Catalyst study - San Diego Freeway.

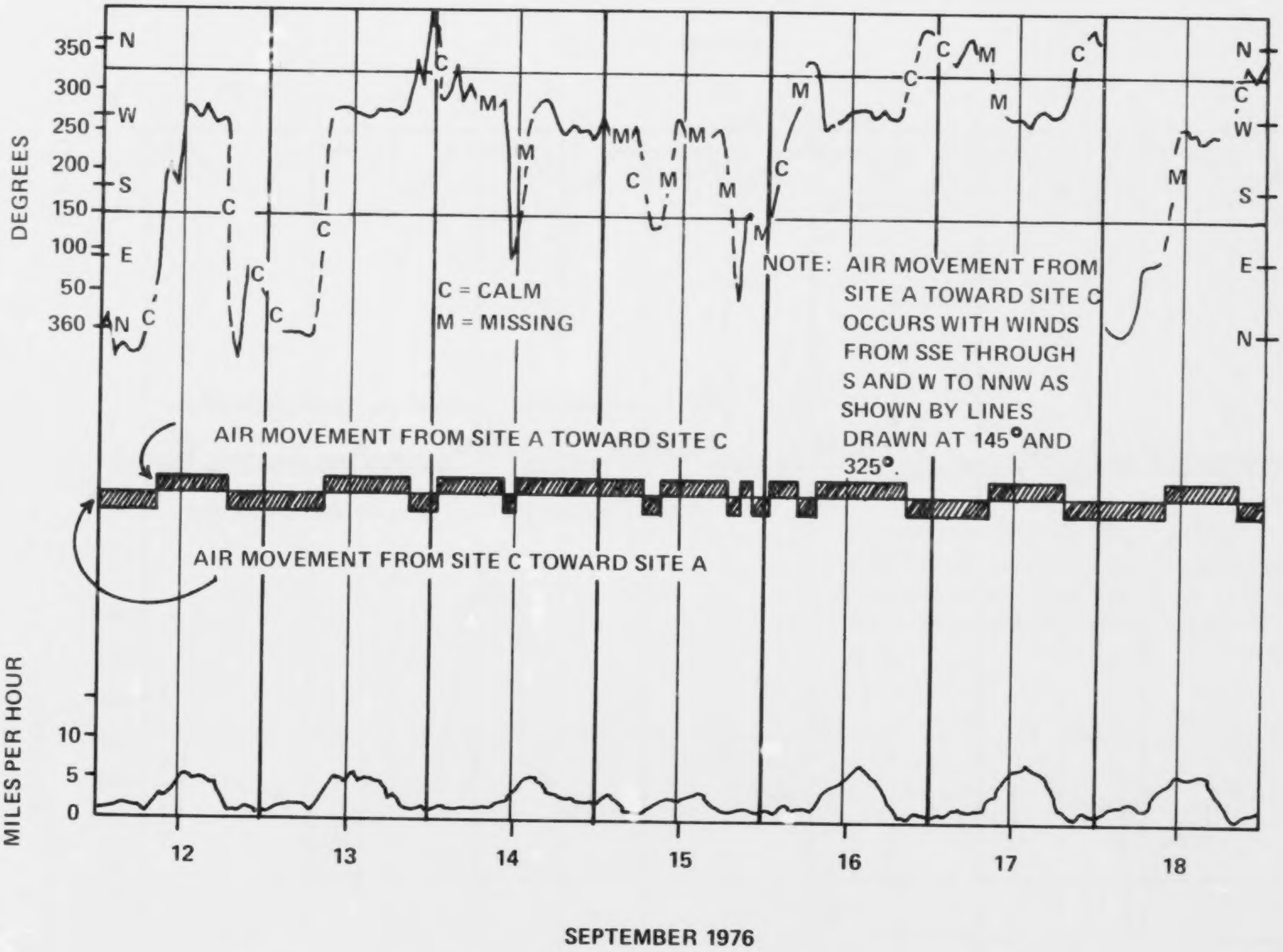


Figure 2. Wind data - Los Angeles Catalyst study - San Diego Freeway.

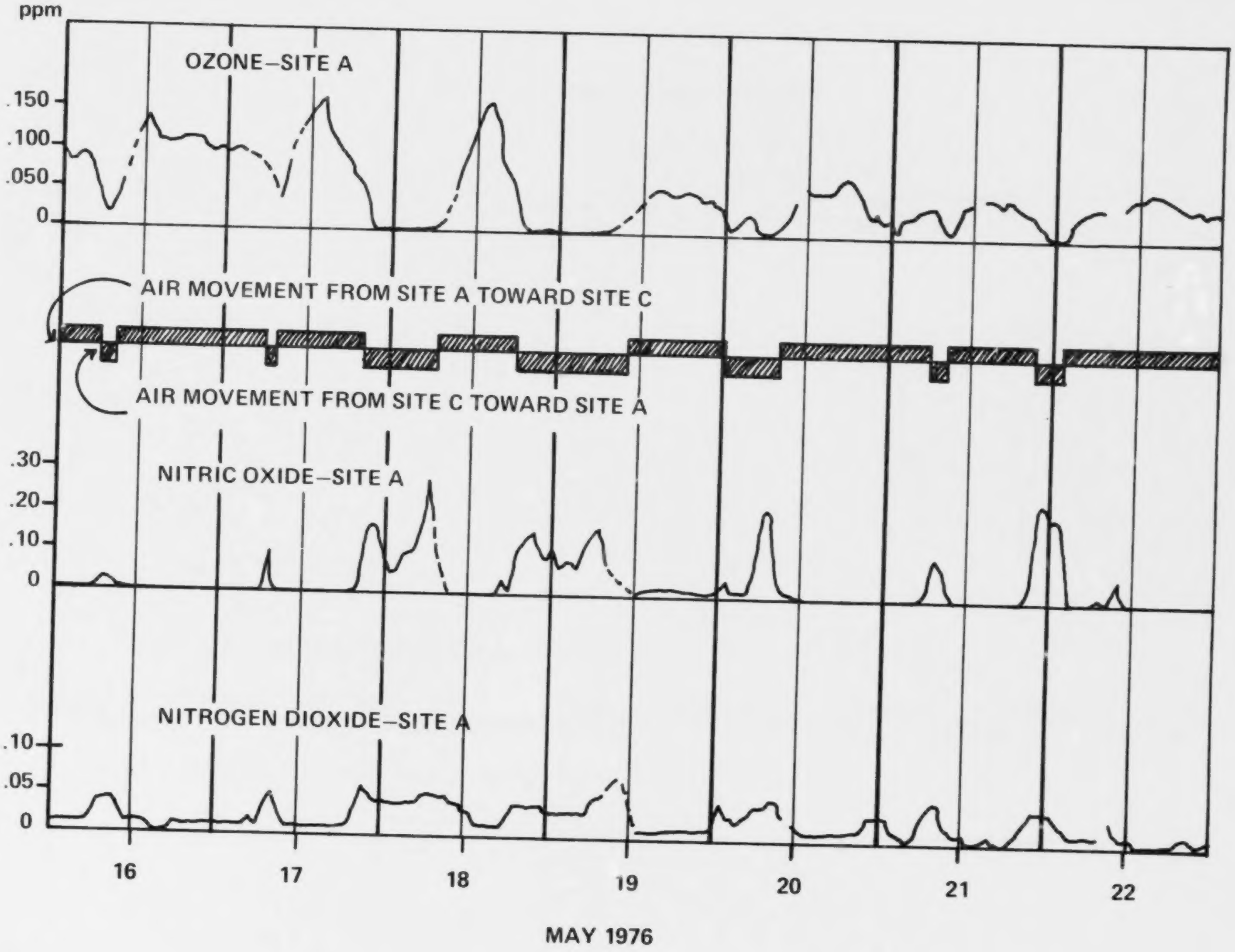


Figure 3. Los Angeles Catalyst study - San Diego Freeway.

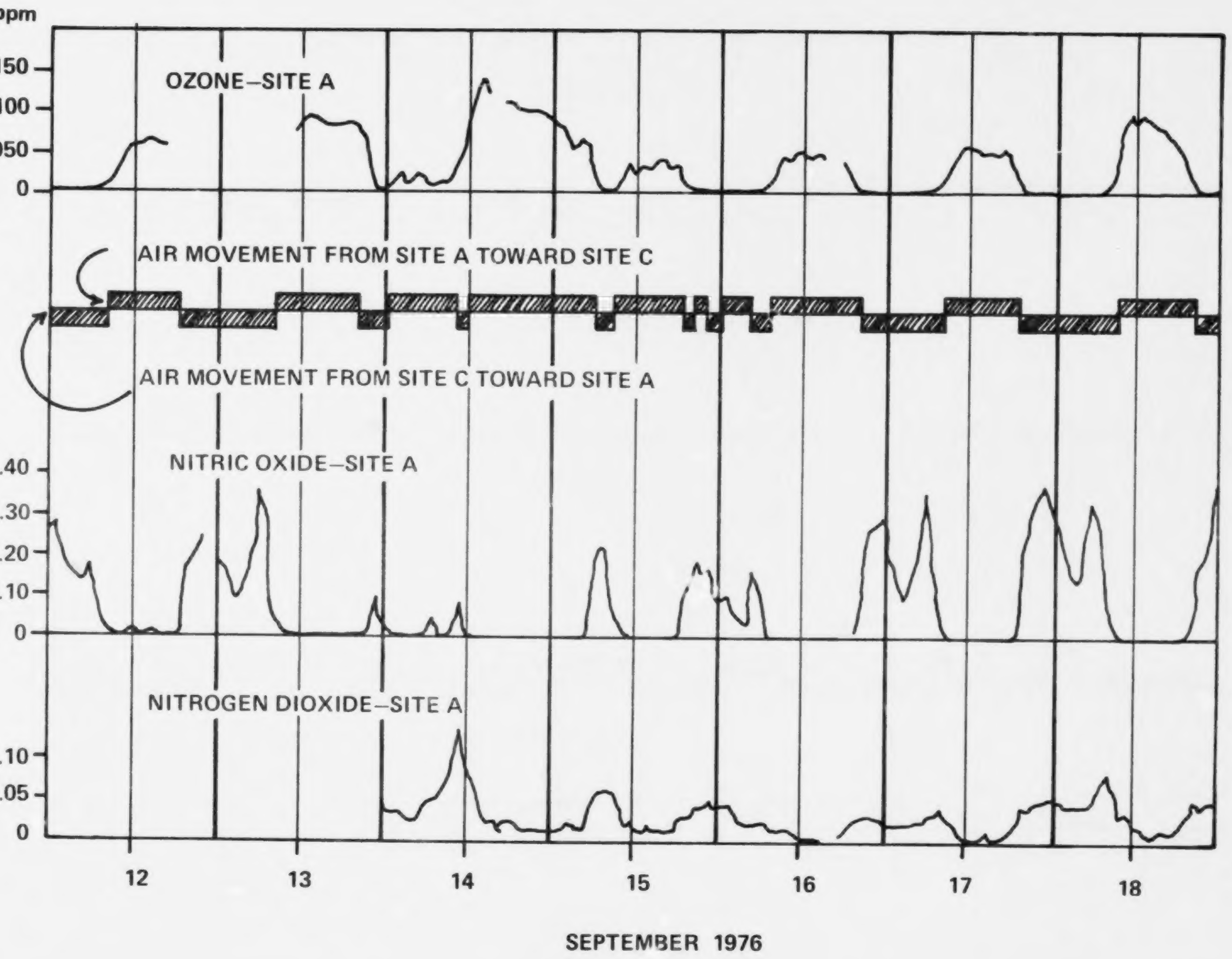


Figure 4. Los Angeles Catalyst study - San Diego Freeway.

of the O_3 measured at the surface may be from O_3 held over from the day before and part is from precursors emitted currently upwind of the Freeway (1). During the late morning and afternoon hours the usual wind direction is from the ocean toward the Freeway. Since the distance from the ocean to the Freeway is about 4 miles (6.4 km) and the wind speed 5 to 8 mph, the time enroute is from around an hour to as little as 30 minutes from the most distant point. This is a fairly short "cooking time" for a large amount of O_3 to be formed, yet out of the 14 days considered there were 6 which had concentrations over the national standard of .08 ppm.

With winds from site C to site A the O_3 concentration at A is almost always zero. This is partly because winds from C to A usually occur at night or early morning when O_3 concentrations are generally low. It is also because the NO from the exhaust gases reacts with O_3 and destroys it before it reaches A. The NO concentration at site A is very dependent on the wind direction. Unless the wind direction is from C to A there is seldom any NO recorded at site A which indicates there is very little background NO. NO_2 concentrations also vary with wind direction, following somewhat the same pattern as NO. However there seems to be some background NO_2 so the concentration seldom goes to zero for long.

At site C (Figures 5 and 6) the concentrations of NO and NO_2 seldom go to zero, but O_3 is usually at zero or close to it. The concentrations of NO vary with traffic volume, and with wind direction, along with other variables which are not so evident. Changes is atmospheric stability undoubtedly change the rate of dispersion. Ozone in the air coming across the Freeway reacts with some of the NO. There always seems to be an excess of NO at site C except perhaps during the hours of least traffic around 0300 or 0400. The production of NO_2 by the reaction of NO with O_3 causes the concentration pattern of NO_2 at site C to follow the concentration pattern of O_3 at site A during the times of winds from A to C. There seems to be a base value of NO_2 perhaps indicating the amount emitted directly in the exhaust gases. The peak concentrations of NO_2 during the middle of the day contrasts with our usual concepts in that the data from our Continuous Air Monitoring Program (CAMP) stations (for instance) show NO_2 as highest shortly after the morning peak of traffic declining to very low afternoon values.

The low traffic volume (Figure 7) at 0300 to 0400 affects the concentration of NO at both A and C. The wind direction is often from C to A at that time of the morning (see September 12, 13, 17, 18). The dip in traffic is reflected in the dip in NO as measured at site A. Other variations in concentration are probably due to differences in wind speed and differences in diffusion due to changes in air stability and/or changes in traffic speed. Changes in traffic speed would surely affect the strength of the eddies in and around the roadway.

These data should be very interesting to modelers even though the study was not designed with modelling in mind.

The data show that NO and O_3 react quickly and increase the concentration of NO_2 as also occurs in the smog chambers. As the emmissions vary the concentrations vary. As the wind changes the concentration pattern shifts. The

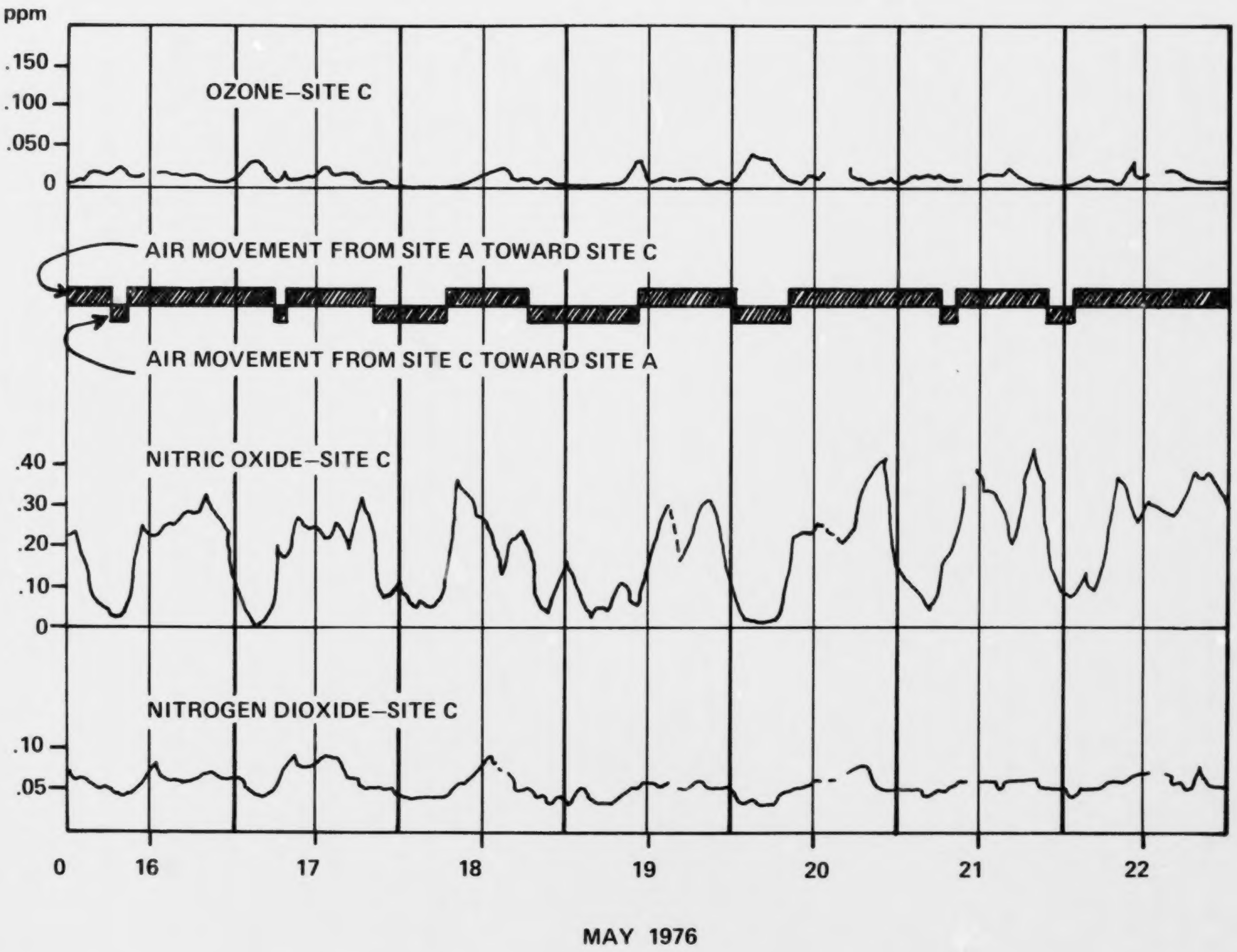


Figure 5. Los Angeles Catalyst study - San Diego Freeway.

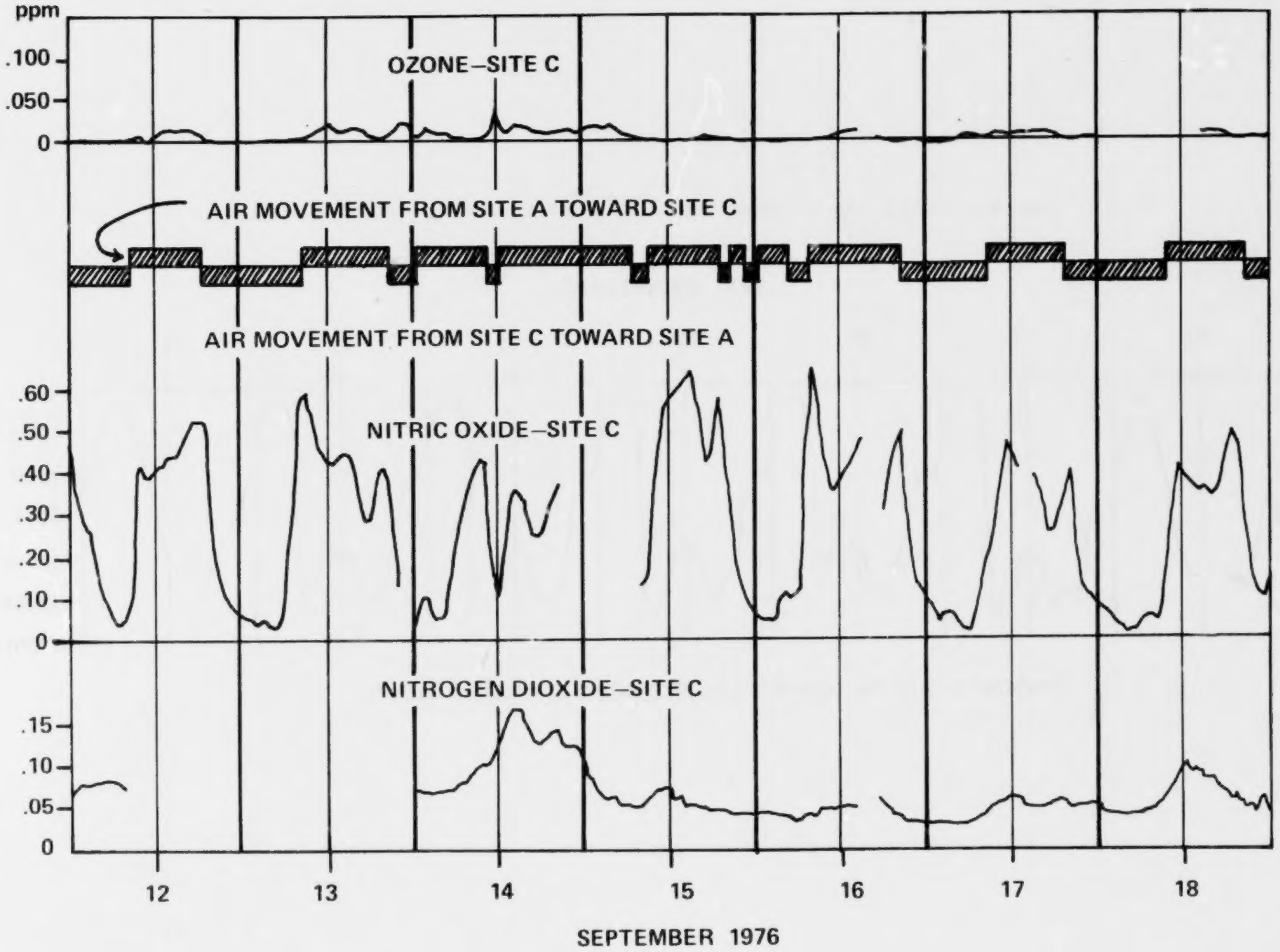


Figure 6. Los Angeles Catalyst study - San Diego Freeway.

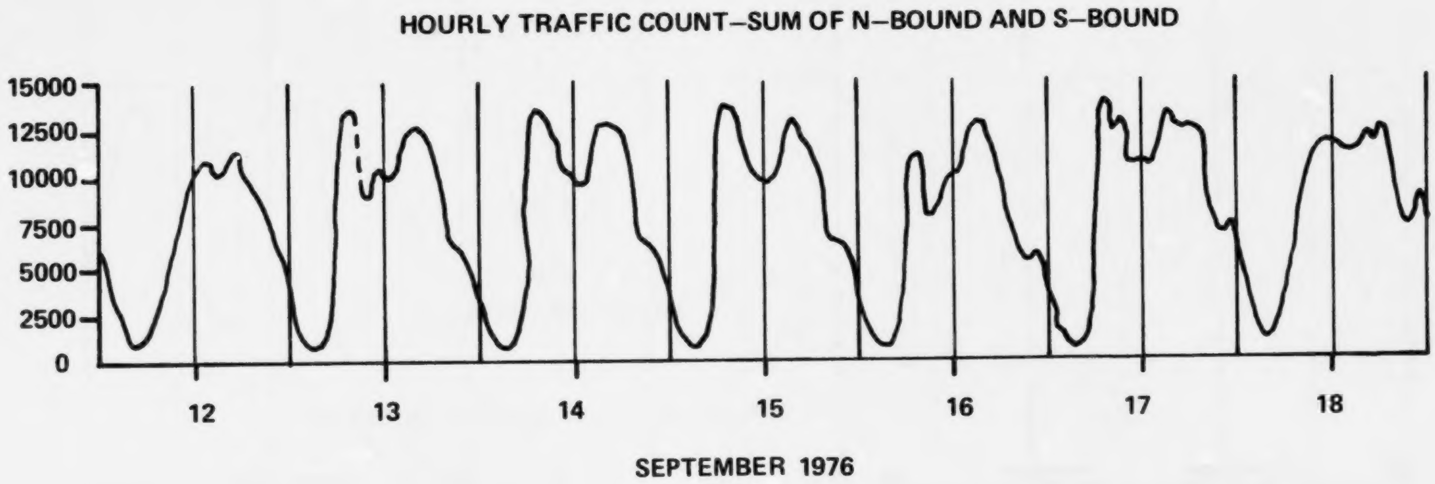


Figure 7. Los Angeles Catalyst study - San Diego Freeway.

traffic count shows that the modeler must definitely allow for different emission patterns on weekends even though the mid-day volume is close to that of weekdays. All this is shown graphically by the accompanying figures.

REFERENCES

1. Coffey, P. E. and W. H. Stasiuk, "Evidence of Atmospheric Transport of Ozone into Urban Areas." New York State Department of Environmental Conservation Publication No. ES4-85, April 1974.

APPENDIX

Because it is important that those who use data know what it represents, a brief description is appropriate of the procedure followed in transforming the analog wind record to a set of numerical values.

Compass Directions read from 0° to 360°. The convention has been adopted that 0 is used only for calm. North is never 0°, but is always 360°. Figure A-1 illustrates some of the problems in determining the proper figure to use in describing the wind direction during a particular hour.

As an example, in figures A-1 and A-2, during the hour from 01 to 02 the wind blew generally from the NW for a little over 30 minutes and then shifted to WSW and stayed in that approximate direction for 20 minutes. The direction which should be recorded for the hour is NW or 315°. The reason the data for the rest of the hour is disregarded is explained below.

Consider pollution as being emitted in short puffs. A puff emitted at time 0100 would move toward the SE for approximately 35 minutes as shown in figure A-1. Then it would move toward the ENE for 25 minutes and arrive at point C. (It is simpler to consider that the wind makes an abrupt shift). The resultant wind direction (287°) would be shown by the line AC and the resultant wind speed would be 6.7 mph. This would be an appropriate figure (rounded off to 290°) to record if we were only interested in the single puff of pollutant emitted at 0100. Any other puff during the hour, as for instance one emitted at 0110 shown by the dotted lines would miss the point C entirely. Usually in air pollution we are interested in places closer to the source of pollution and also in continuous emissions. If we consider points within about 2 miles of the source it can be seen that at D pollution would be blowing past that point for 35 minutes and past F for 25 minutes. Any point along any direction in between would receive pollution only momentarily as the plume swung past. Therefore only NW or WSW are readily to be considered and NW must be chosen since it would have received the pollution for a longer period of time.

The illustrations in figure A-2 show other examples. In the time period from 00 to 01 the wind is from the NW for less than 20 minutes, but a receptor along any other radius would have received pollution for a much lesser time, so NW is the best choice. We must remember that in this case a sampler which depends on cumulative collection, even if it was in the most favored direction would have received pollution for only a third of the hour, so a strong source might appear weak. Pollution from a point source would be weakened by the changeability of the wind between 02 and 03 even though the wind stayed in SW sector.

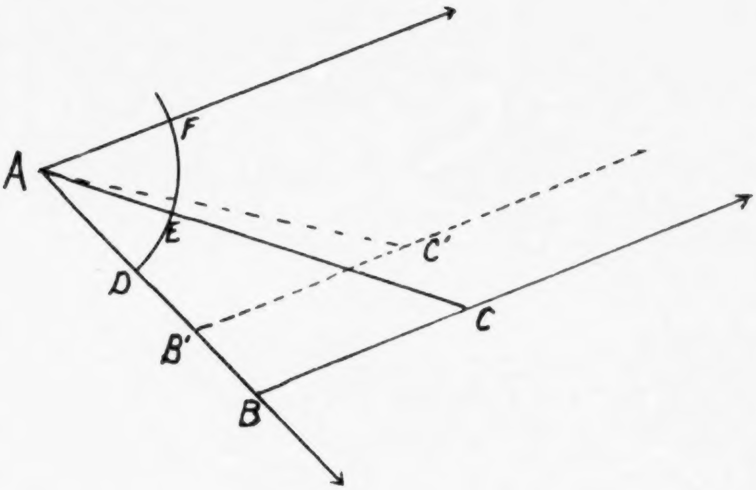
For a line source such as the San Diego Freeway small changes in the wind *direction are not as important unless the wind happens to be nearly parallel to the line source so that the transport across the Freeway is switched from one side to the other.*

As long as the air transport is from the line source toward the sampling site any wind direction will blanket the receptor downwind of a line source.

For sites close to the line source there is an increase in concentration of pollutants when the wind becomes nearly parallel to the line, at least if the line source is effectively infinite in length. With a line source the lowest concentrations are received at a receptor site which is on a line perpendicular to the line source, however up to 45° deviation from the perpendicular makes only a small difference. (1)

REFERENCE

1. *D. B. Turner, "Line Source Modeling" Proceedings of the Fifth Metting of the NATO/CCMS Expert Panel on Air Pollution Modeling, June 4-6, 1974, Roskilde, Denmark. August 1974*



AB represents a NW wind at 8 mph for 35 minutes
BC   "   " WSW " " 8 mph " 25   "
AC   "   the resultant wind direction and speed

AB' represents a NW wind at 8 mph for 25 minutes
B'C'   "   " WSW " " 8 mph " 25 minutes
AC'   "   the resultant wind direction and speed

Figure A-1. Wind direction schematic.

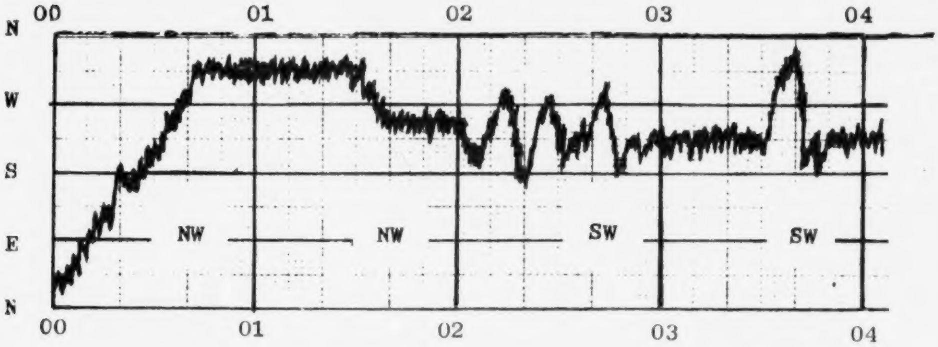


Figure A-2. Hourly wind direction.

SUMMARY OF LACS INTEGRATED POLLUTANT DATA

Charles E. Rodes and Gary F. Evans

Environmental Protection Agency
Research Triangle Park, North Carolina

ABSTRACT

This paper is a continuation of the discussion of measurements made at the Los Angeles Catalyst Study site from June 1974 through December 1976. The continuous measurements resulting in hourly averages are discussed in a separate report, whereas this summary is concerned with measurements integrated over either 4-hour or 24-hour intervals. With the exception of the sulfur dioxide bubbler, the integrated measurements in this study are generated from aerosol sample analyses. The results described are for total suspended particulates, lead, sulfates, sulfur dioxide, and other related measurements. The aerosol sampler methods discussed include the high-volume sampler, 102 mm membrane sampler, dichotomous sampler, and the 5-stage Andersen cascade impactor sampler. The sulfur dioxide bubbler and the high-volume samplers are operated according to Environmental Protection Agency reference method procedures. The long-term data trends of each of the pollutants are described as well as the interrelationships of pollutant combinations. In general the data indicate decreases in the freeway contributions of total suspended particulates and lead since 1974, but only a very small positive contribution of sulfates.

INTRODUCTION

The samplers operated at the Los Angeles Catalyst Study (LACS) for the collection of aerosols and sulfur dioxide (SO_2) are operated over selected intervals. The time intervals utilized are either a 24-hour interval from midnight to midnight, or a 4-hour interval during the evening rush hour from 1500-1900 hours. The aerosol samplers utilize either filters or impaction plates to collect the aerosol materials, while the SO_2 is collected using the reference West-Gaeke Method.

Specifications for the aerosol samplers used in the LACS are given in Table I. The four types of samplers are (1) the standard high-volume (hi-vol) sampler specified in the Federal Register; (2) the membrane sampler (RAC 2349 or equivalent); (3) the dichotomous sampler (ERC Model 200 or equivalent); and (4) the 5-stage Andersen cascade impactor with back-up filter. Operation of a variety of methods provides sample collection over a range of aerosol size, plus information on method comparability.

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TABLE I. LACS AEROSOL SAMPLER SPECIFICATIONS

	FILTER MATERIAL	FILTER SIZE mm	FLOWRATE m^3/min	SIZE RANGE μ
HI-VOL	GLASS FIBER	200 X 250	1.4	<100μ
MEMBRANE	CELLULOSE ESTER	102	0.14	<100μ
DICHOTOMOUS*	TEFLON	37	0.014	<2.5μ
CASCADE BACK-UP	CELLULOSE ESTER	102	0.14	<0.7μ

* "FINE" CHANNEL ONLY. SAMPLER ALSO HAS "COARSE" AND "TOTAL" CHANNELS, 2.5 – 10μ AND <10μ RESPECTIVELY.

The hi-vol sampler utilizes specially selected acid-washed glass fiber filters and is designed to collect Total Suspended Particulates (TSP) defined as less than 100 microns. The membrane sampler was designed to be an aerodynamic equivalent of the hi-vol also collecting TSP, but utilizing a membrane filter substrate at one-tenth the flowrate. The aerosol collection capabilities of this sampler have not been adequately defined, but it is felt this sampler also does not quantitatively collect particles greater than 30 microns.

The dichotomous samplers used in the LACS are special prototype versions of the two-channel virtual (non-impaction) sampler recently made commercially available. These prototype samplers have a third "Total" channel in addition to the "Coarse" and "Fine" channels. After the prototypes were placed in the field, it was subsequently determined that the "Coarse" and "Total" channels suffered losses of the larger particles making these channels unreproducible. Fortunately the "Fine" channel, which collects particles in the important size fraction less than 2.5 microns, operated properly. The analysis information in this report described as "Dichotomous" refers only to this "Fine" particle fraction.

Five-stage Andersen cascade impactors are used to provide information about not only the mass size distribution of the TSP aerosols, but also the distribution by size of selected analytes. The Andersen sampler is essentially a membrane sampler with a 5-stage impactor added above the filter. Therefore, the membrane filter acts as a back-up stage collecting particles less than approximately 0.7 micron.

The integrated samplers at the LACS as previously mentioned operate over either a 4-hour or 24-hour period. The results discussed in this report were compiled from June 1974 thru December 1976 and represent a substantial number of samples collected. Table II lists the types of integrated samples, the number of valid samples collected, and the analyses performed on each sample. Note that the membrane and dichotomous samples are also analyzed by X-Ray Fluorescence Spectrometry (XRF) to obtain selected elemental analyses.

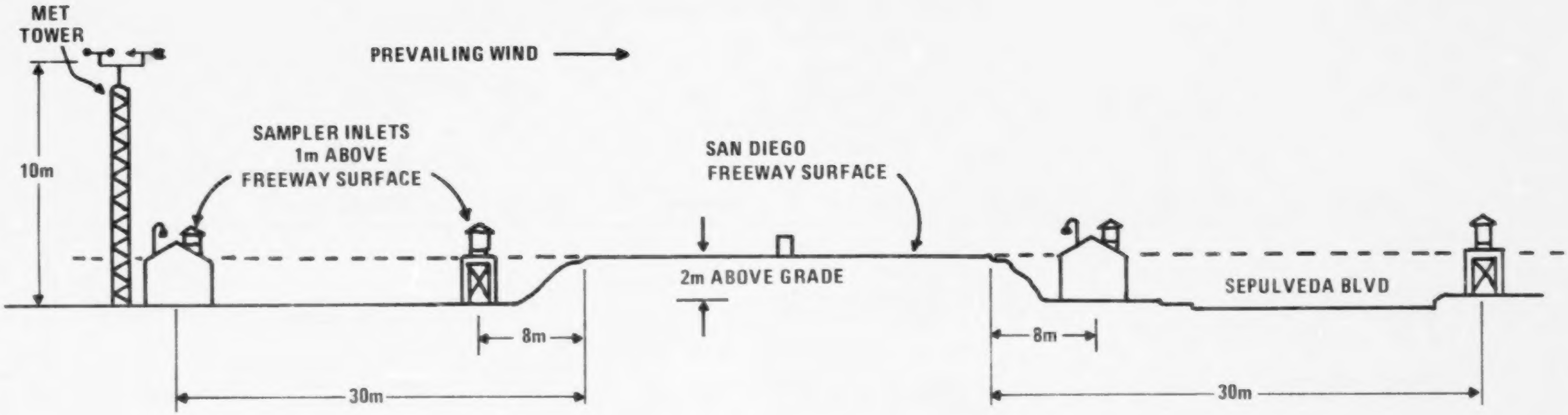
The integrated samplers are located at the sites shown in the elevation in Figure 1. The majority of the samplers are located at Sites A and C, with only hi-vols and membranes operated at Sites B and D. Sites A and B are typically "Upwind" of the freeway because of the prevailing wind direction, and Sites C and D are "Downwind." The freeway contribution of a selected constituent is determined by subtracting the measurement at Site A from the measurement at Site C. The samples collected at Sites B and D provide spatial distribution information and, to a lesser degree, freeway contribution information when the wind is blowing opposite to the prevailing direction. Note that Site A is a "background" site unaffected by the freeway during the 1500-1900 hour period, but cannot be considered as a background site over a 24-hour period because of shifting winds.

The integrated samplers are operated according to the schedule shown in Figure 2. Again, the greatest concentration of measurements are made at Sites A and C, with daily collection of 24-hours hi-vols and 4-hour hi-vols and membranes. The SO_2 bubblers are also operated at Sites A and C on a 24-hour

TABLE II. INTEGRATED SAMPLES COLLECTED AT LACS

	# Samples Collected	% Valid	# Valid Samples	Analyses
24-hr Hi Vols	2280	90.4	2061	TSP, Pb, $SO_4^=$, NO_3^-, NH_4^+
4-hr Hi Vols	3420	94.9	3246	TSP, Pb, $SO_4^=$, NO_3^-, NH_4^+
24-hr Membrane	570	88.7	506	Same as Hi-Vol plus XRF*
4-hr Membrane	1270	96.2	1222	Same as Hi-Vol plus XRF*
24-hr Dichotomous	555	76.9	427	Mass, $SO_4^=$, NH_4^+, H^+, XRF*
24-hr Cascade Backup	470	81.5	383	Mass, XRF*
24-hr SO_2 Bubbler	1710	89.3	1527	SO_2

*Elemental analyses by XRF include S, Pb, Br, Ca, Si, Fe, Zn, Al, and Cl.


MET TOWER
10m
PREVAILING WIND
SAMPLER INLETS 1m ABOVE FREEWAY SURFACE
SAN DIEGO FREEWAY SURFACE
2m ABOVE GRADE
SEPULVEDA BLVD
8m
8m
30m
30m

SITE A

CO ANALYZER
TOTAL SULFUR (SO_2) ANALYZER
NO/NO_2 ANALYZER
O_3 ANALYZER

24-HR SO_2 BUBBLER

24-HR HI-VOL
4-HR HI-VOL (3-7 PM)
4-HR MEMBRANE (3-7 PM)
24-HR CASCADE
MASSIVE VOLUME AIROSOL SAMPLER
24-HR DICHOTOMOUS SAMPLER

AMBIENT TEMP. AND DEWPOINT
WIND SPEED
WIND DIRECTION

SITE B

24-HR HI-VOL
4-HR HI-VOL (3-7 PM)
24-HR MEMBRANE

SITE C

CO ANALYZER
TOTAL SULFUR (SO_2) ANALYZER
NO/NO_2 ANALYZER
O_3 ANALYZER

24-HR SO_2 BUBBLER

24-HR HI-VOL
4-HR HI-VOL (3-7 PM)
4-HR MEMBRANE (3-7 PM)
24-HR CASCADE
MASSIVE VOLUME AEROSOL SAMPLER
24-HR DICHOTOMOUS SAMPLER

TRAFFIC SPEED AND COUNT SYSTEM

SITE D

24-HR HI-VOL
4-HR HI-VOL (3-7 PM)
24-HR MEMBRANE

Figure 1. LACS study site composition and elevation.

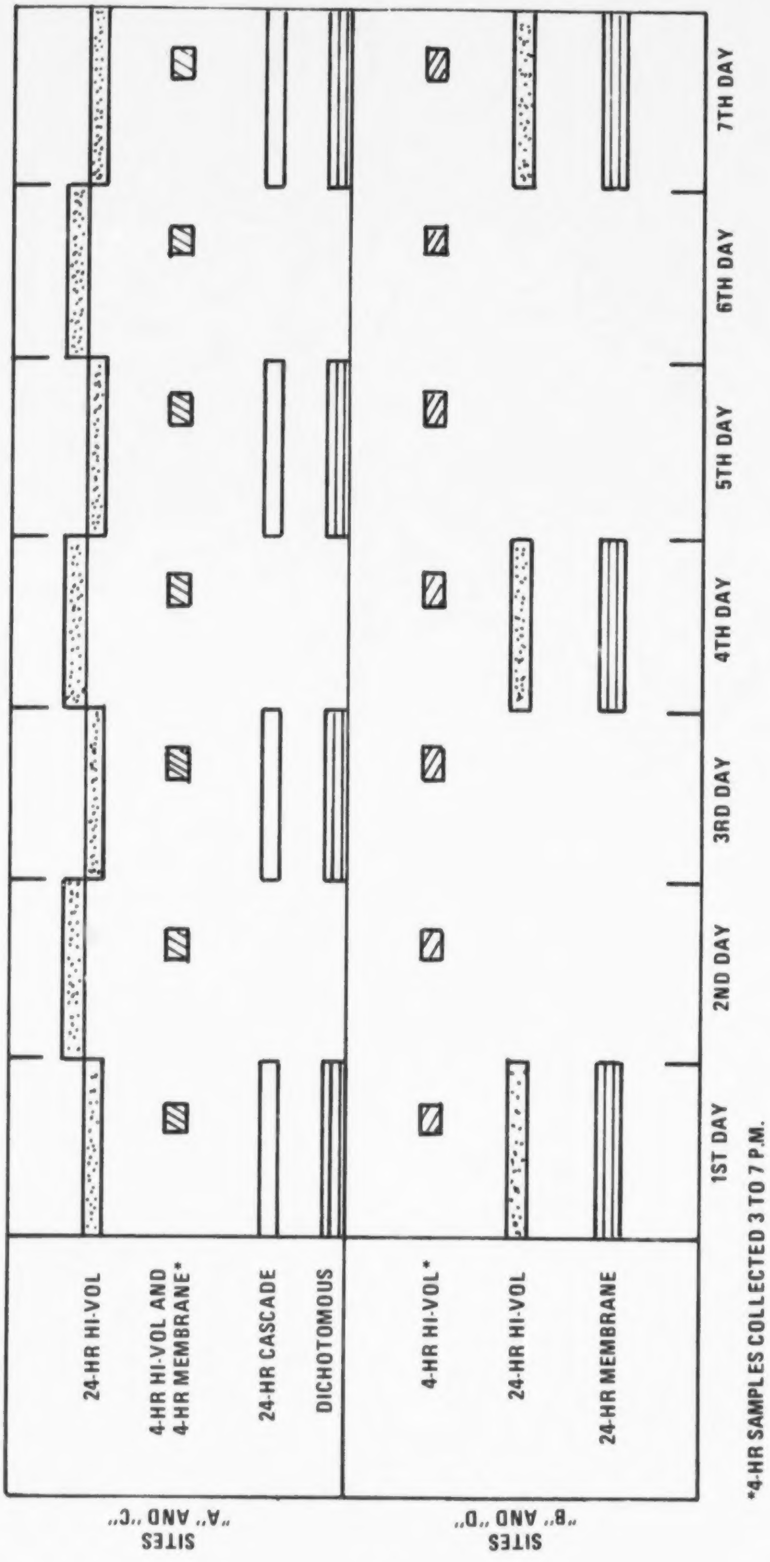

SITES "A" AND "C"
24-HR HI-VOL
4-HR HI-VOL AND 4-HR MEMBRANE*
24-HR CASCADE
DICHOTOMOUS
SITES "B" AND "D"
4-HR HI-VOL*
24-HR HI-VOL
24-HR MEMBRANE
1ST DAY
2ND DAY
3RD DAY
4TH DAY
5TH DAY
6TH DAY
7TH DAY
*4-HR SAMPLES COLLECTED 3 TO 7 P.M.

Figure 2. LACS platform sampler schedules.

basis. The every-other-day and every-third-day operation schedule for the other samplers was dictated by the resources available to provide long-term trend information.

CONCLUSIONS

The results presented here represent only a portion of the integrated sample analyses collected at the LACS. This paper describes only those results which are the most significant in terms of the original study objective to examine long-term trends. The results presented include measurements for TSP, lead (Pb) and sulfate ($SO_4^=$).

The most important conclusions based on the LACS integrated measurements through 1976 are as follows, not necessarily in order of importance:

(1) The background levels of TSP and Pb (approximately 85 $\mu g/m^3$ and 0.5 $\mu g/m^3$, respectively) have changed very little since the beginning of the study.

(2) The background level of $SO_4^=$ has decreased 25% since 1974.

(3) The freeway contributions during the evening rush hour (1500-1900) of TSP and Pb have both decreased 25% since 1975, whereas the contribution of $SO_4^=$ from the freeway is small and has only recently become measureable above background. The average 1500-1900 hour contributions of TSP and Pb during the summer of 1976 were 44 $\mu g/m^3$ and 7 $\mu g/m^3$, respectively.

(4) The consensus of methods indicates only 0.5 to 1.0 $\mu g/m^3$ freeway contribution of $SO_4^=$ during periods of favorable meteorology.

(5) Artifact sulfate formation on hi-vol samples does not appear to be significant in determining 24-hour cross-freeway $SO_4^=$ differences, but apparently contributes a substantial error to 4-hour hi-vol sulfate measurements.

TOTAL SUSPENDED PARTICULATES AND MASS DATA

The data presented in previous LACS quarterly and semi-annual reports have been shown graphically on a monthly basis. The freeway contribution for 1975 and 1976 of TSP as measured by the hi-vol at Sites A and C from 1500-1900 hrs is shown in Figure 3 on a monthly basis. This graph can be erroneously interpreted, however, because of the varying meteorology from month-to-month. Since the wind speed and direction are not uniform on a monthly basis, the freeway contribution calculation varies, depending on the magnitude of the resultant wind vector. Examination of the meteorology by month shows a definite seasonality in the favorable wind direction sector preferred for determining cross-freeway differences. Table III summarizes the meteorology by "Summer" and "Winter" (April thru September and October thru March, respectively) seasons, and shows an average of 95.9% favorable wind directions during the "Summer" (1500-1900 hour interval). The percentage during the

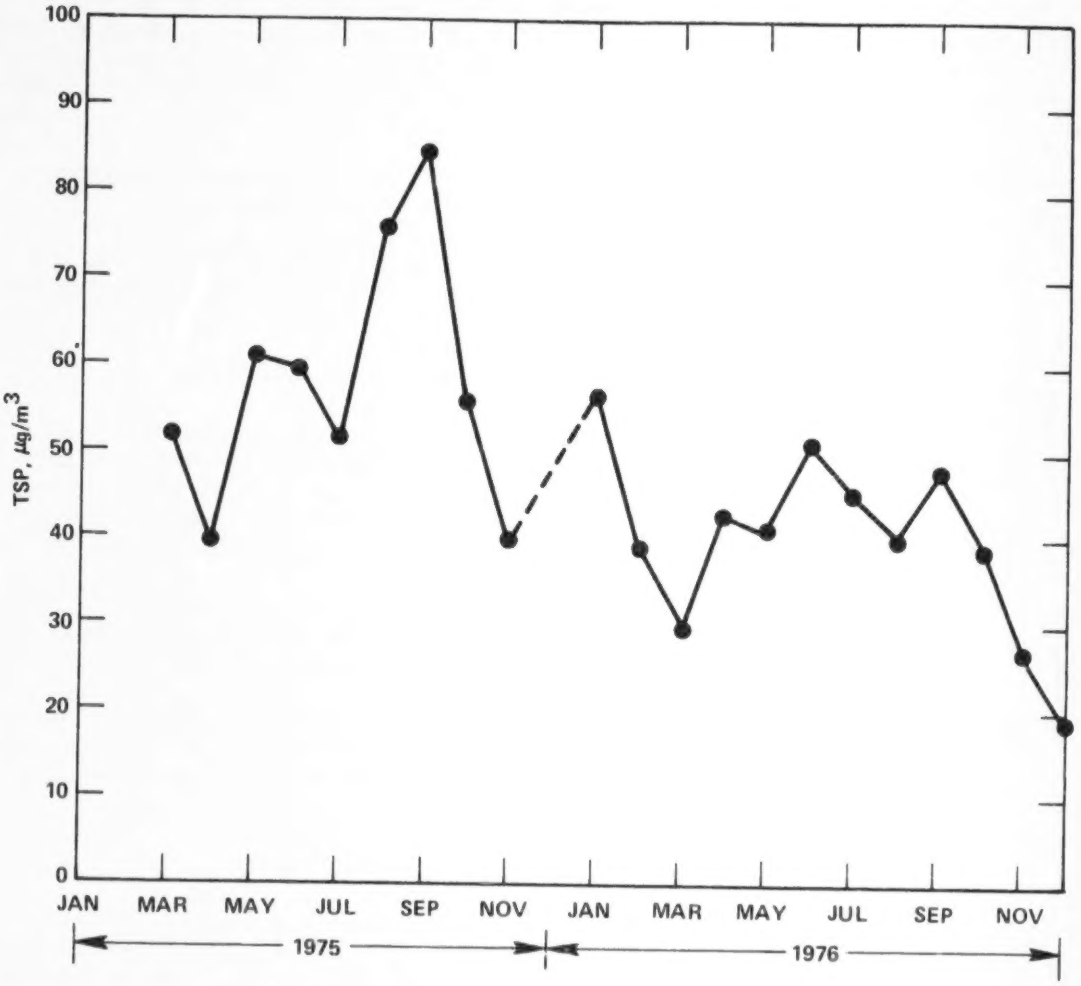


Figure 3. 1500-1900 hr freeway contribution of TSP, hi-vol (C-A).

TABLE III. AVERAGE PERCENT FREQUENCY FROM S+SW+W AND THE ASSOCIATED AVERAGE SPEED BY SEASON AND SAMPLING INTERVAL

Season[a]	Sampling Interval			
	15-19 hr		0-24 hr	
	% WD (S+SW+W)	Avg WS, mph	% WD (S+SW+W)	Avg WS, mph
Summer, 1974[b]	96.6	5.1	63.6	3.5
Winter, 1974	61.9	4.2	34.9	3.7
Summer, 1975	96.6	5.5	62.3	3.6
Winter, 1975	70.0	4.2	39.5	3.8
Summer, 1976	94.7	5.2	58.9	3.5
Winter, 1976[c]	32.7	3.1	28.1	3.0
Average[d] Summer	95.9	5.3	61.4	3.5
Average[d] Winter	59.3	4.0	35.4	3.6

[a] Summer - April thru September;
Winter - October thru March

[b] Season began June 1, 1974

[c] Season ended December 15, 1976

[d] Weighted

"Winters" drops to 59.3%. Note especially that even during "Summer" seasons the 24-hour interval is only slightly more favorable than the "Winter" 1500-1900 hour period. These less favorable conditions result in a larger upwind level at Site A and consequently a smaller freeway contribution based on the C minus A difference over a 24-hour period. The atypically poor meteorology in the winter of 1976 makes interpretation of results in this period very difficult.

When the data in Figure 3 are averaged on a seasonal basis to reduce the effect of meteorology, the results are as shown in Figure 4. This plot also includes 1974 data, and provides a much clearer picture of the long-term trends in TSP contribution by the freeway. Note the slight increases in the summer seasons as compared to the winter seasons caused by the more favorable meteorology. If the summer seasons alone are examined to virtually eliminate the effect of meteorology, the results are as shown Figure 5. From this plot it is apparent that the overall freeway contribution has decreased substantially from 1974 to 1976. The total decrease has been approximately 40% of which 25% has occurred from 1975 to 1976. Membrane samplers, as mentioned earlier, are also operated at the LACS to provide comparison information with other methods. The hi-vol and membrane data agree in trend and on the average differ by only about 10 $\mu g/m^3$ with the hi-vol giving larger values. It is important to remember that each of the points on this graph is an average of 150-180 samples and the error bands, if applied to each point would be very small.

Examination of the "background" particulate trends as measured upwind at the LACS shows only a slight decrease in Figure 6 from 1974 to 1976 by a consensus of 4 different methods. The dichotomous sampler "Fine" fraction is approximately 1/3 of the TSP values of both the hi-vol and membrane. The TSP background of approximately 90 $\mu g/m^3$ shows the effect of meteorology by reducing during the summer seasons the influence of the freeway on the "background" sites. During the 4-hour period from 1500-1900 hours the more favorable meteorology removes the freeway influence on the upwind site.

On a 24-hour basis (Figure 7) the freeway contributions of TSP and mass are approximately 1/3 those during the 1500-1900 hour interval, because of less favorable meteorology and lower average emission rates. The effect of less favorable meteorology becomes very pronounced on a 24-hour basis, showing the summer values to be approximately twice those during the winter. Figure 8 shows this information on a summer-only basis and indicates only a slight decrease in TSP by the hi-vol and no change in the dichotomous "Fine" fraction.

The spatial distributions of TSP by site and sampling interval are shown in Figure 9. This graph indicates that the background TSP on either a 4-hour or 24-hour basis is a substantial fraction of the downwind measurements, and the difference between Sites A and B is small. The comparison between Sites C and D, however, shows a substantial difference between sites and sampling intervals. The decreases from Site C to Site D is caused by both dilution and large particle deposition of the freeway contribution to the TSP burden.

Utilization of the information from the 24-hour Andersen cascade results in graphs plotting particle size (diameter) versus the cumulative percent

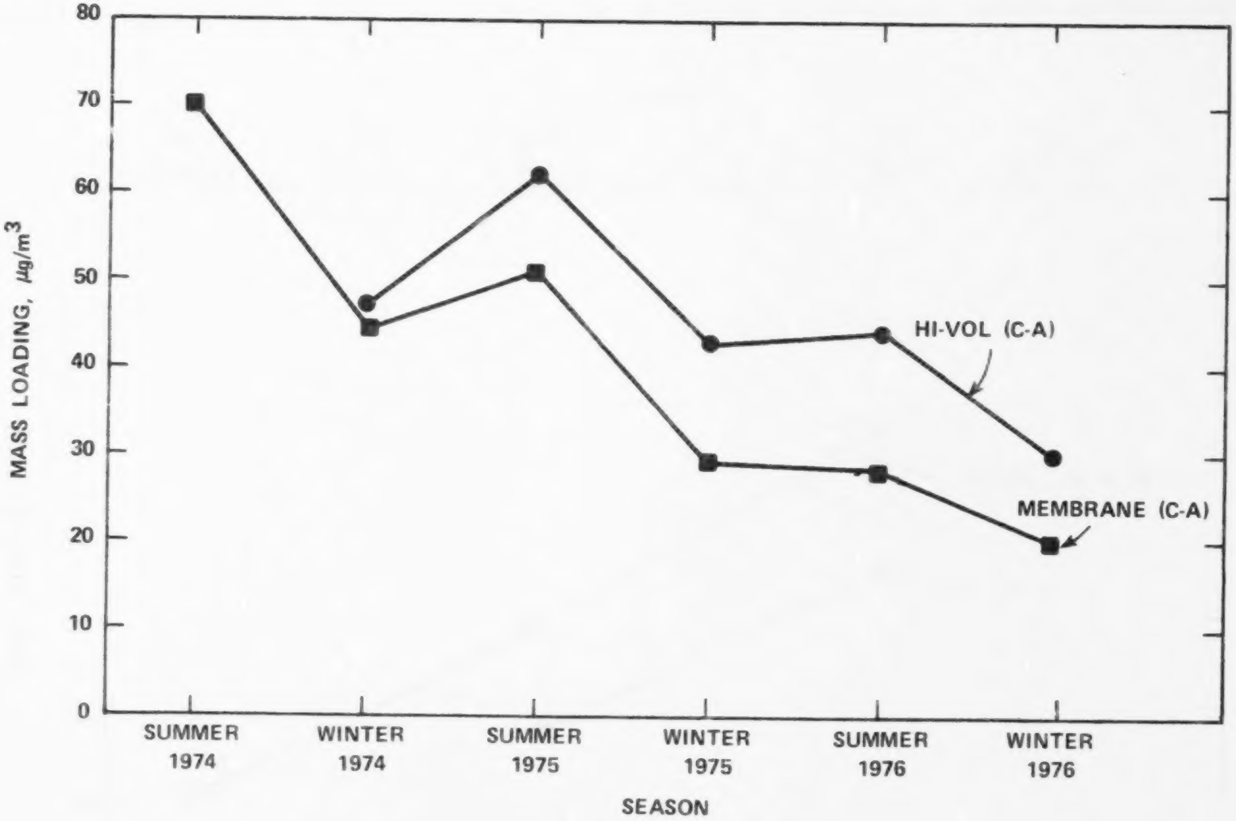


Figure 4. 1500-1900 hr freeway contribution of suspended particulates.

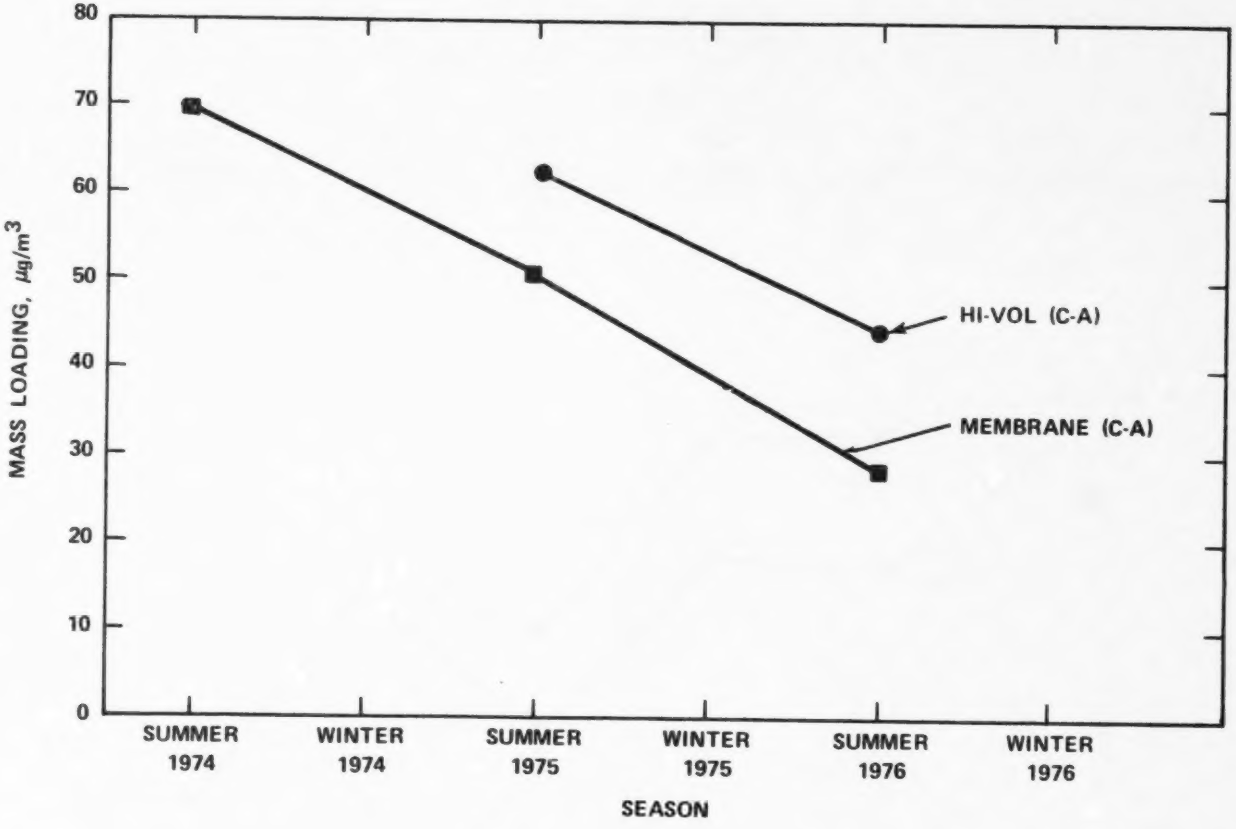


Figure 5. 1500-1900 hr freeway contribution of suspended particulates (summer seasons only).

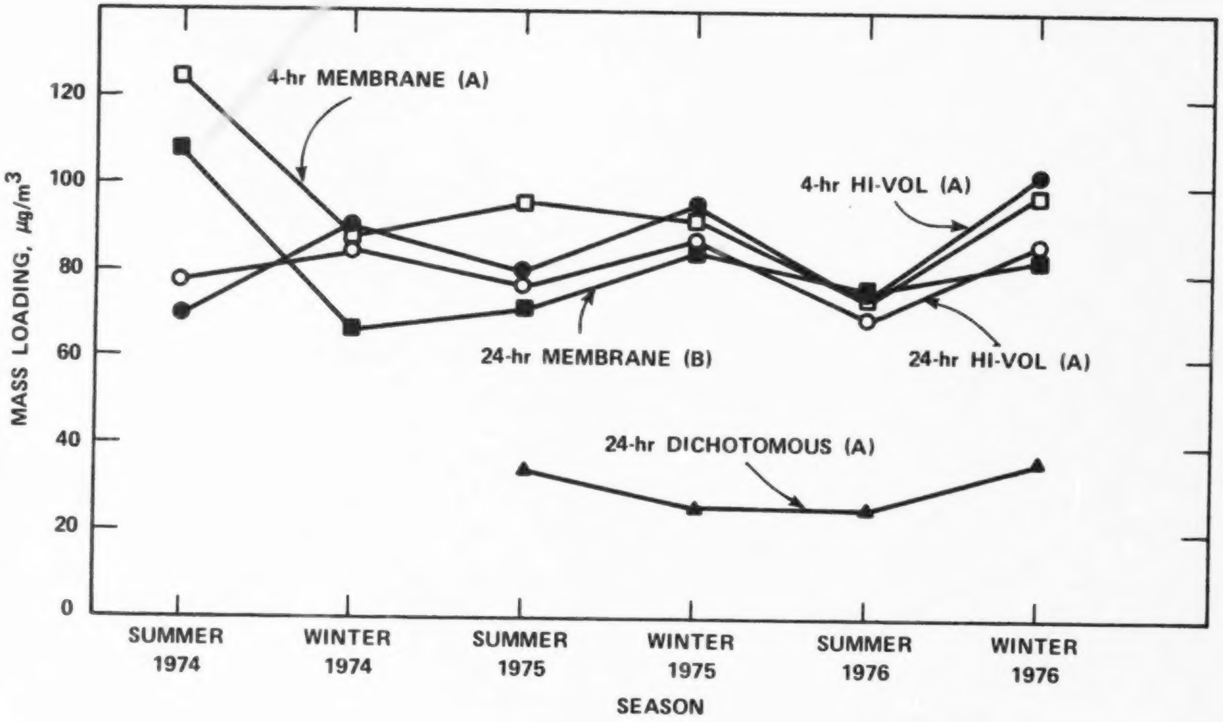


Figure 6. Background suspended particulate trends.

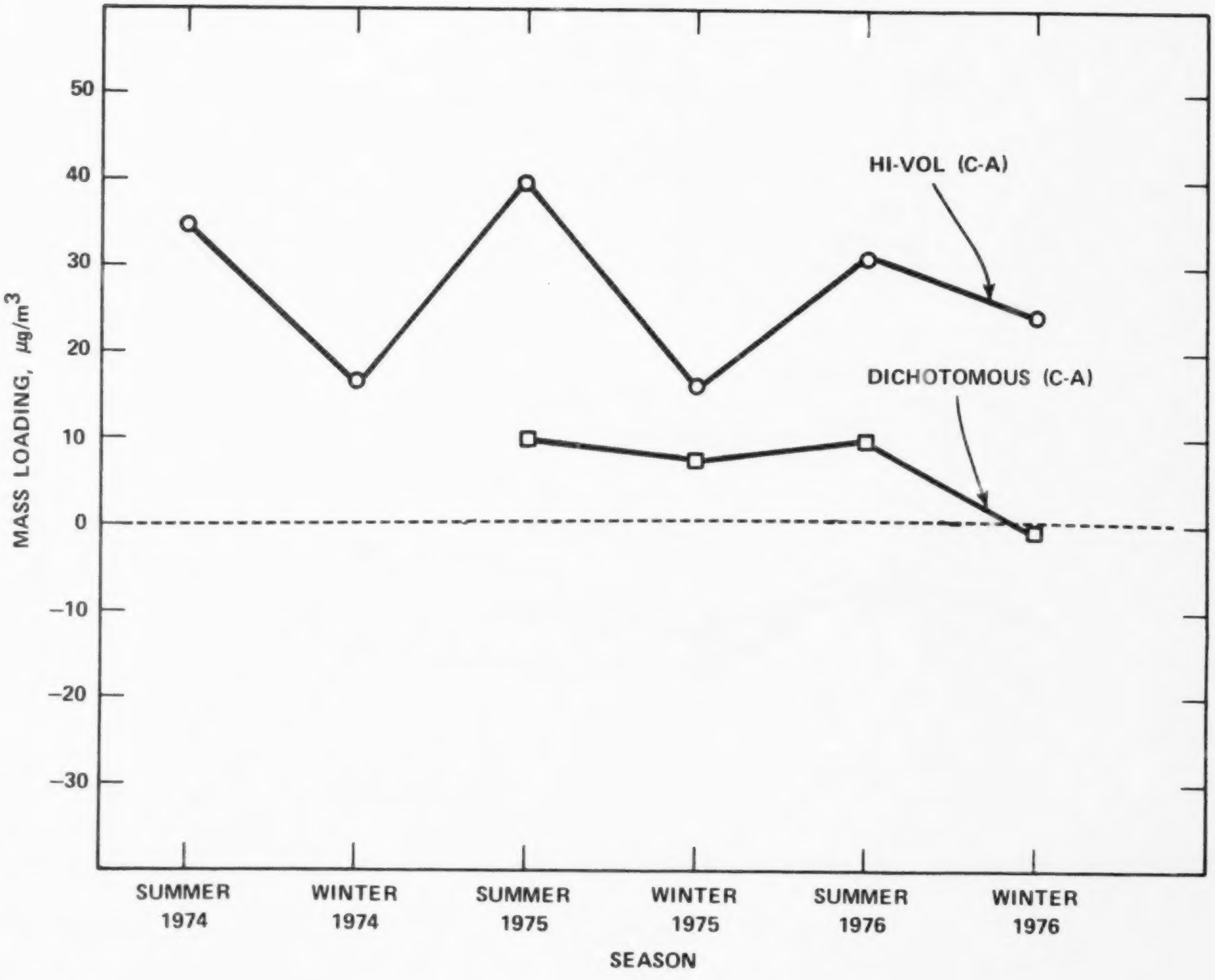


Figure 7. Twenty-four hour freeway contribution of suspended particulates.

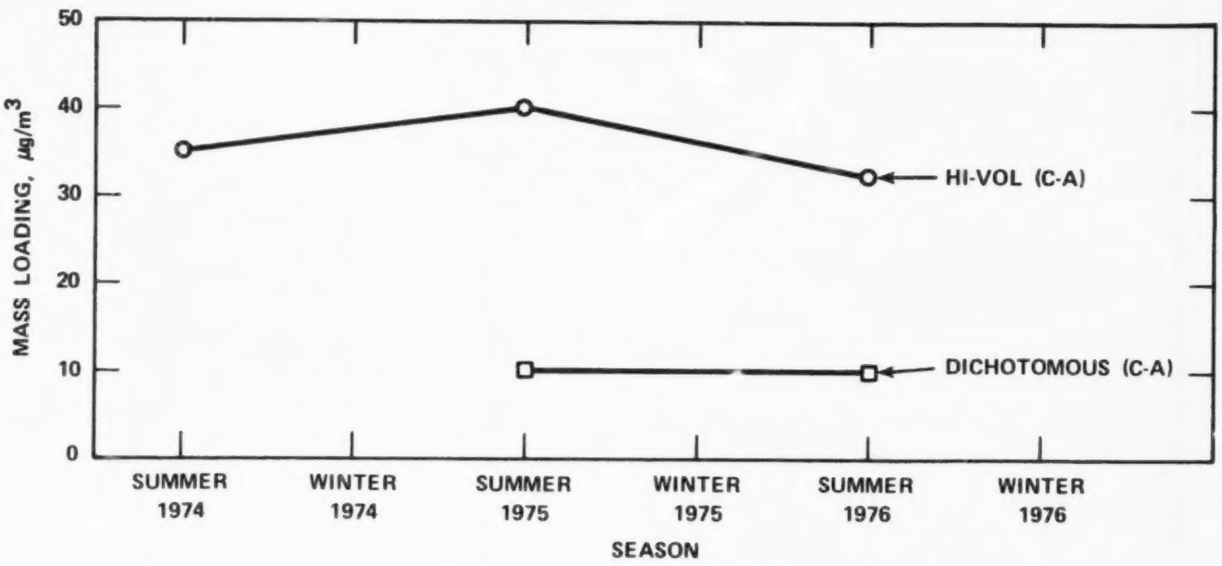


Figure 8. Twenty-four hour freeway contribution of suspended particulates (summer seasons only).

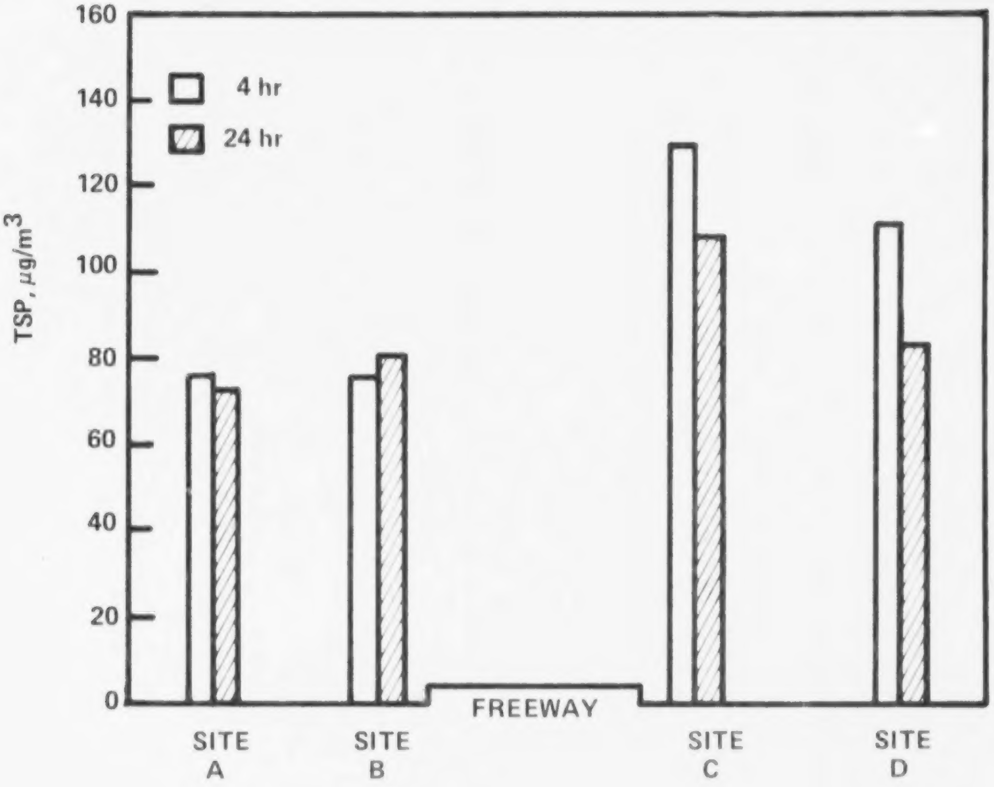


Figure 9. Spatial distribution of TSP by sampling interval (summer seasons).

less-than-or-equal-to a given aerosol size. Figure 10 is a composite of data from samples collected at Sites A and C during the summer of 1975. From this graph it is apparent that the mass is distributed in a log-normal manner at both sites, with a slightly smaller mass median diameter (MMD) at Site C than at Site A. Approximately 50% of the TSP is below 1.0 micron and 80% is less than 2.5 microns.

If the mass median diameters from both sites are plotted by season as in Figure 11, it is obvious that there is a strong seasonality in median particle size. The "Summer" seasons have mass median diameters nearly twice those of the "Winters" due to a combination of factors including particle growth during periods of increased photochemical activity. Overall the average MMD is approximately 0.7 microns.

LEAD DATA

Analysis of Pb data from the aerosol samples collected at the background sites at the LACS shows (see Figure 12) a very strong influence of the freeway during the winter months. This again is the result of unfavorable meteorology. The consensus of methods during the summer months is a background level of less than 1.0 $\mu g/m^3$.

The 24-hour freeway contribution shown in Figure 13 shows a seasonal meteorology effect similar to that of TSP. The "Summer" season values are approximately 3-5 times as great as the "Winter" levels. Examination of the "Summer" seasons in Figure 14 shows that there has been a significant decrease in TSP lead contribution from the freeway as measured by the hi-vol, even as examined on a 24-hour basis. The dichotomous and cascade back-up samples, however, showed only a slight decrease. By sampler type the order of decreasing Pb collected is hi-vol, dichotomous "Fine," and cascade backup. Even though the size of the dichotomous "Fine" fraction (<2.5 microns) is much larger than the cascade-backup fraction (<0.7 micron), there is only a slight difference between amount of Pb collected in each fraction. Further examination of the size distribution of Pb is made in Figure 15 by plotting the results of the summer season Andersen cascade samples composited and analyzed by stage. Note that unlike mass, Pb is not log-normally distributed and shows a strong site dependence. As would be expected the downwind MMD is substantially smaller than the upwind MMD. Also the distribution is somewhat bimodal with a significant fraction of "large" (>2.5 microns) particle Pb, very little between 1.0 and 2.5 microns, and 75% less than 1.0 micron.

If the 1500-1900 hour freeway contribution of Pb is examined in Figure 16, it is noted that only a small seasonal effect is apparent with an average contribution of approximately 7.0 $\mu g/m^3$ Pb above the background. Examination of the summer seasons in Figure 17 shows a marked decrease from 1975 to 1976 of approximately 25%. Even though only two points are shown for each line, a substantial number of data points are averaged to obtain each seasonal value.

The cause of the 25% decrease in Pb was investigated by determining the fraction Pb in the TSP collected. Since the TSP had also decreased, it was felt that the Pb decrease may have caused the decrease in TSP. Figure 18

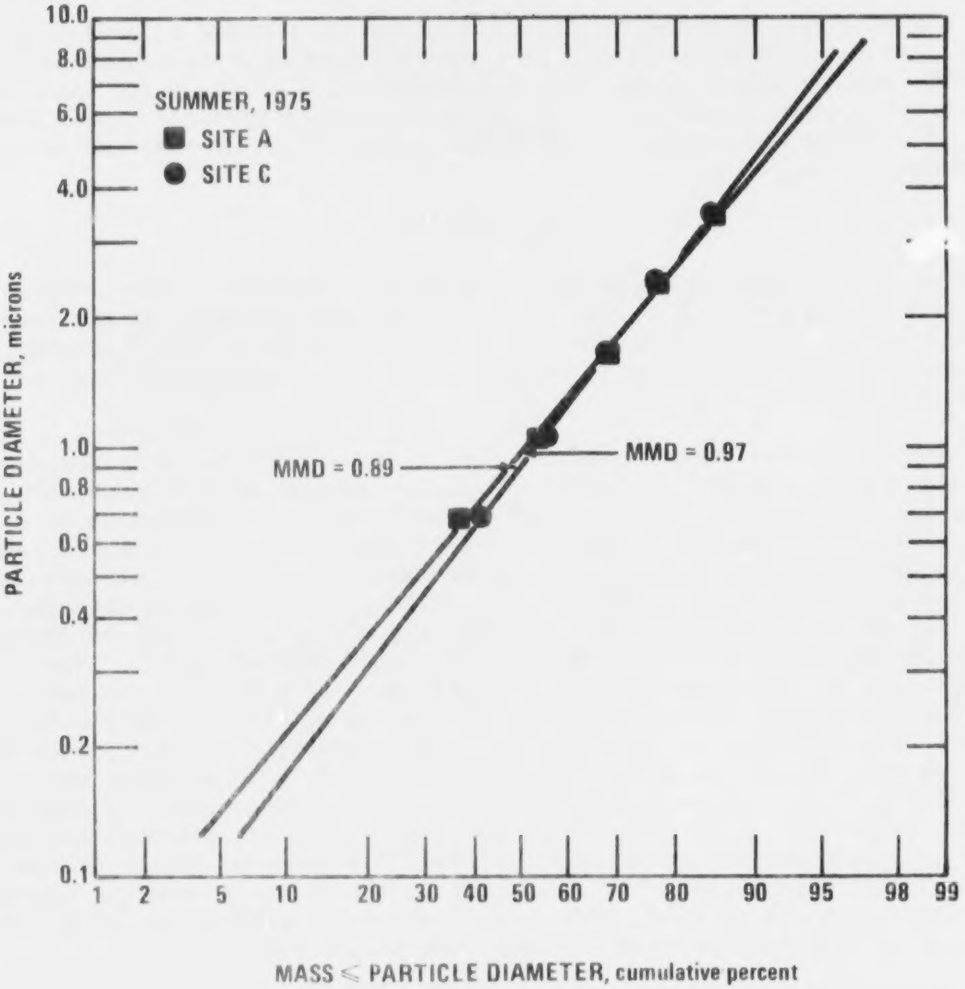


Figure 10. Twenty-four hour cascade composites - mass.

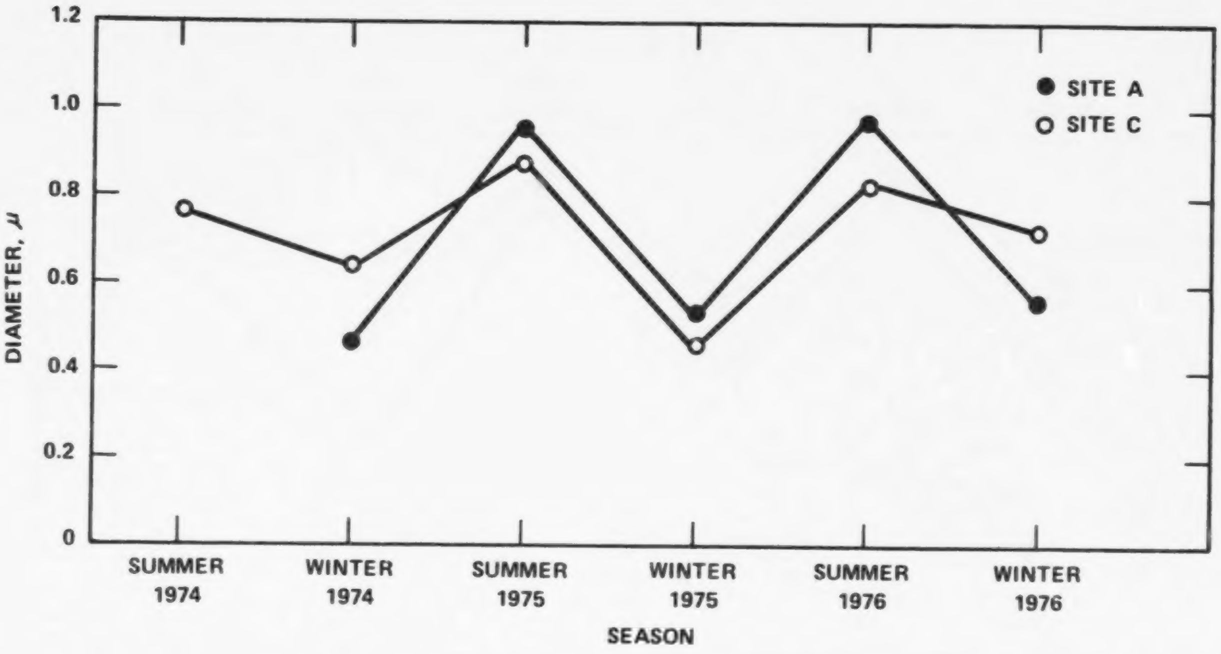


Figure 11. Comparison of 24-hr mass median diameters.

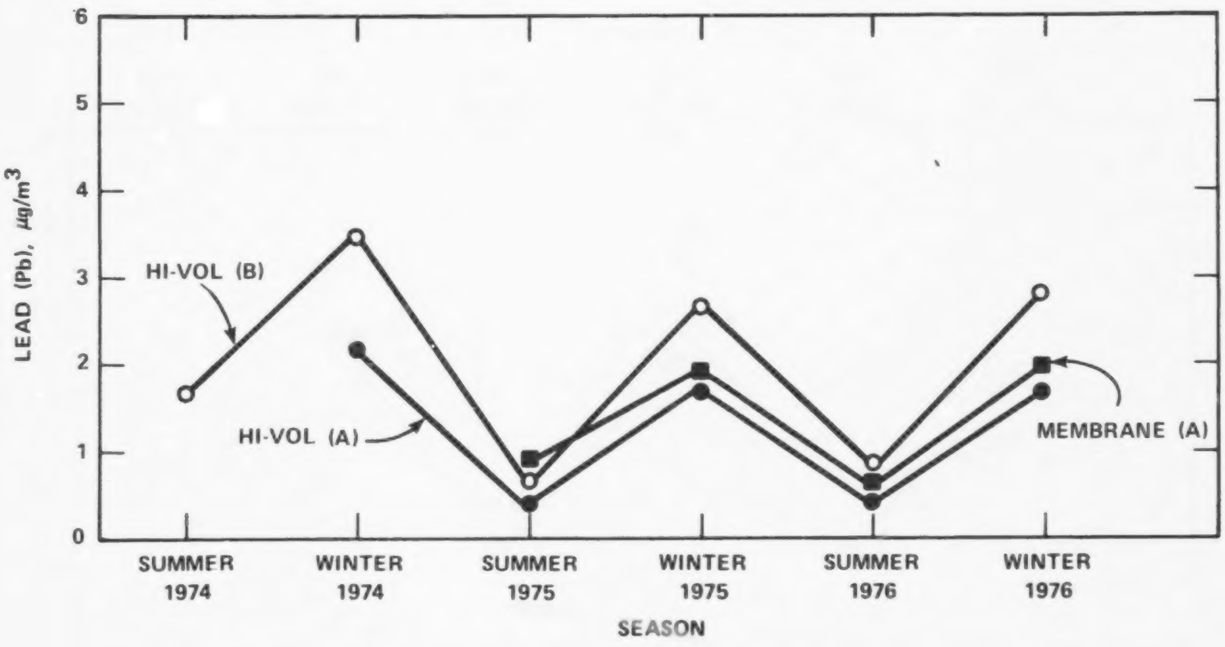


Figure 12. Background lead trends (1500-1900 hr data).

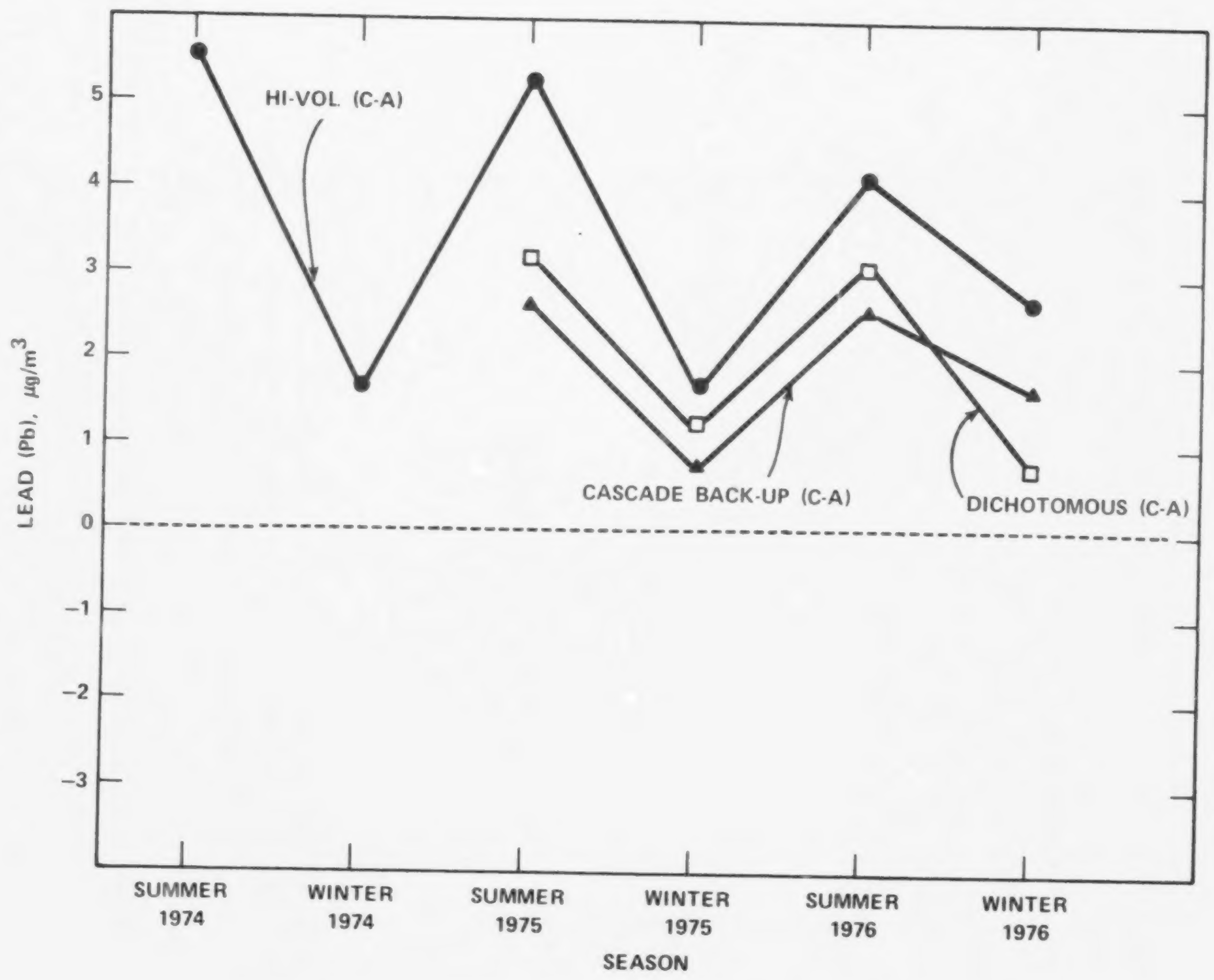


Figure 13. Twenty-four hour freeway contribution of lead.

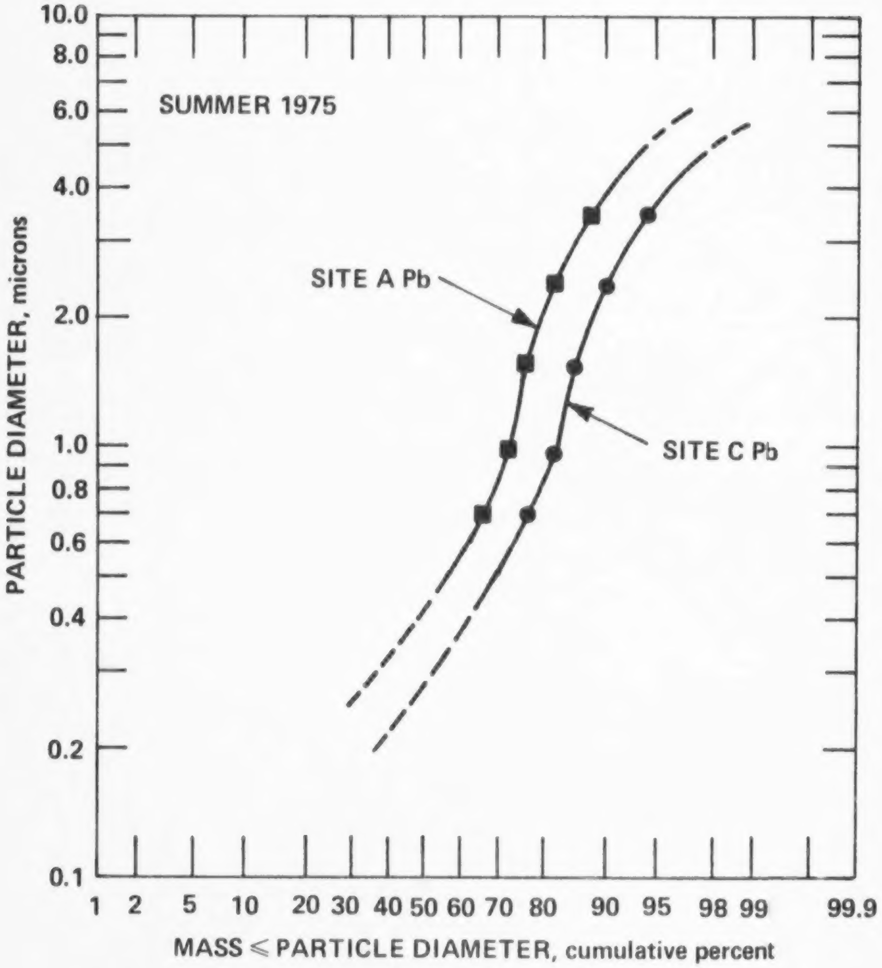


Figure 15. Twenty-four hour cascade composites - Pb.

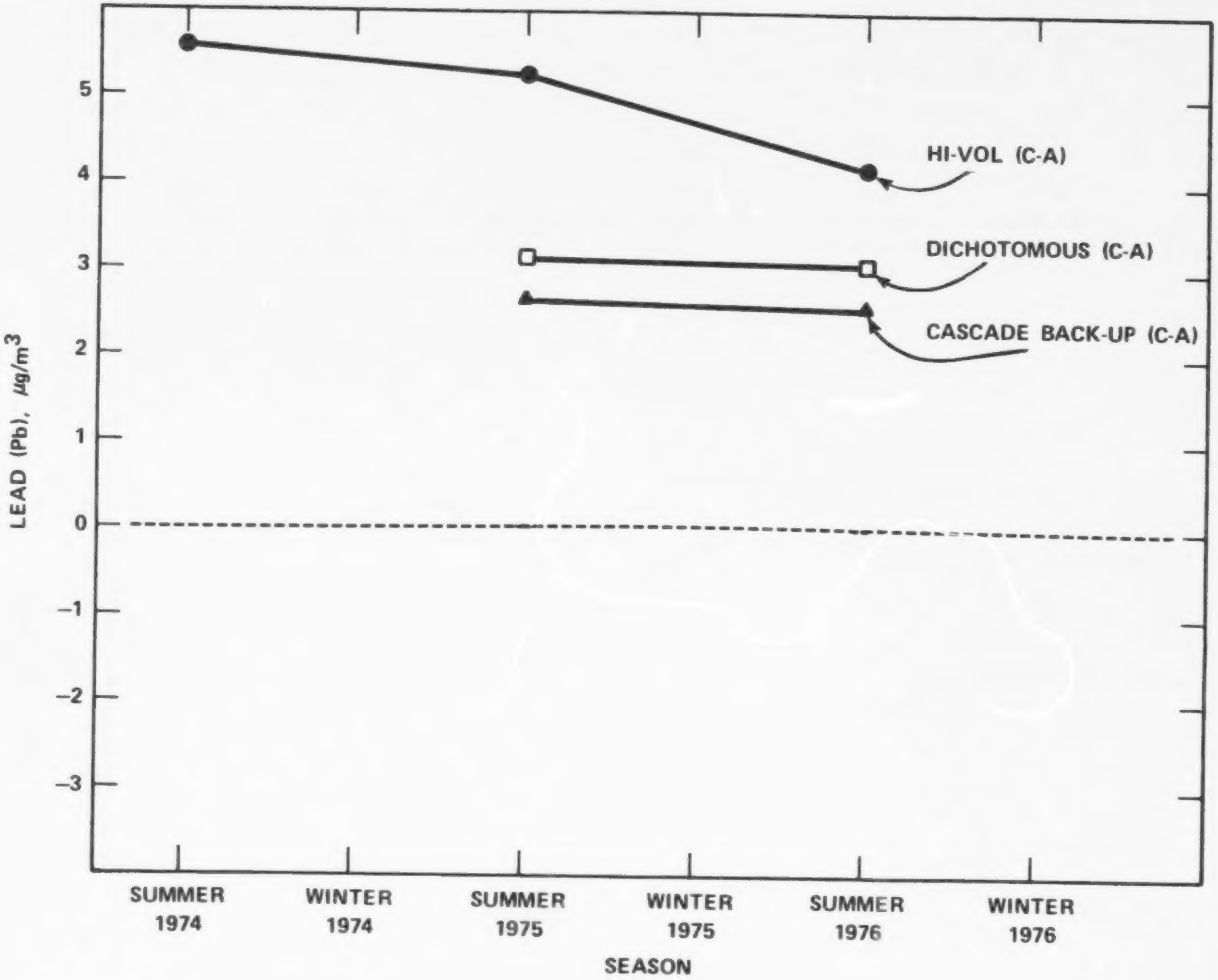


Figure 14. Freeway contribution of lead (summer seasons only).

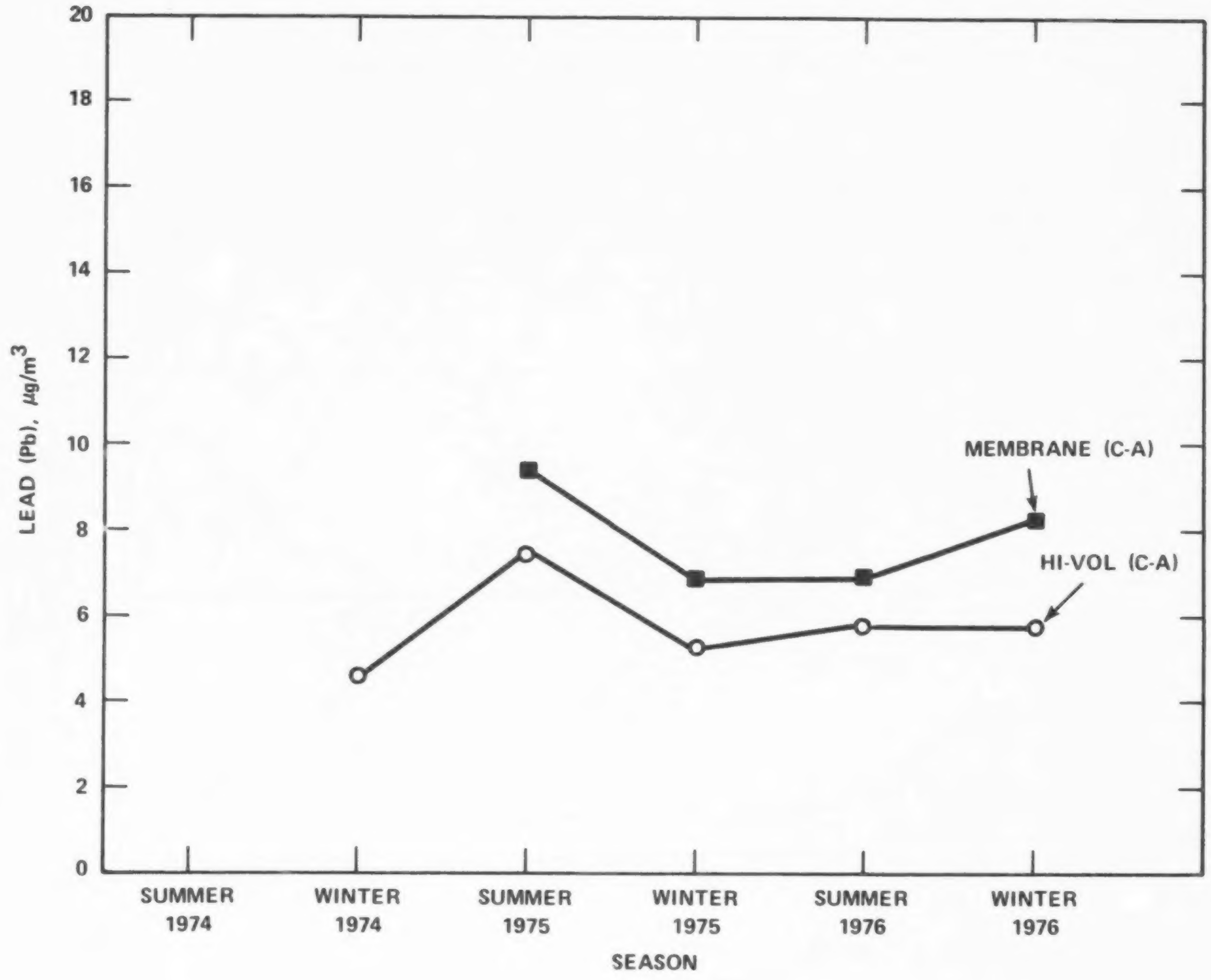


Figure 16. 1500-1900 hr freeway contribution of lead.

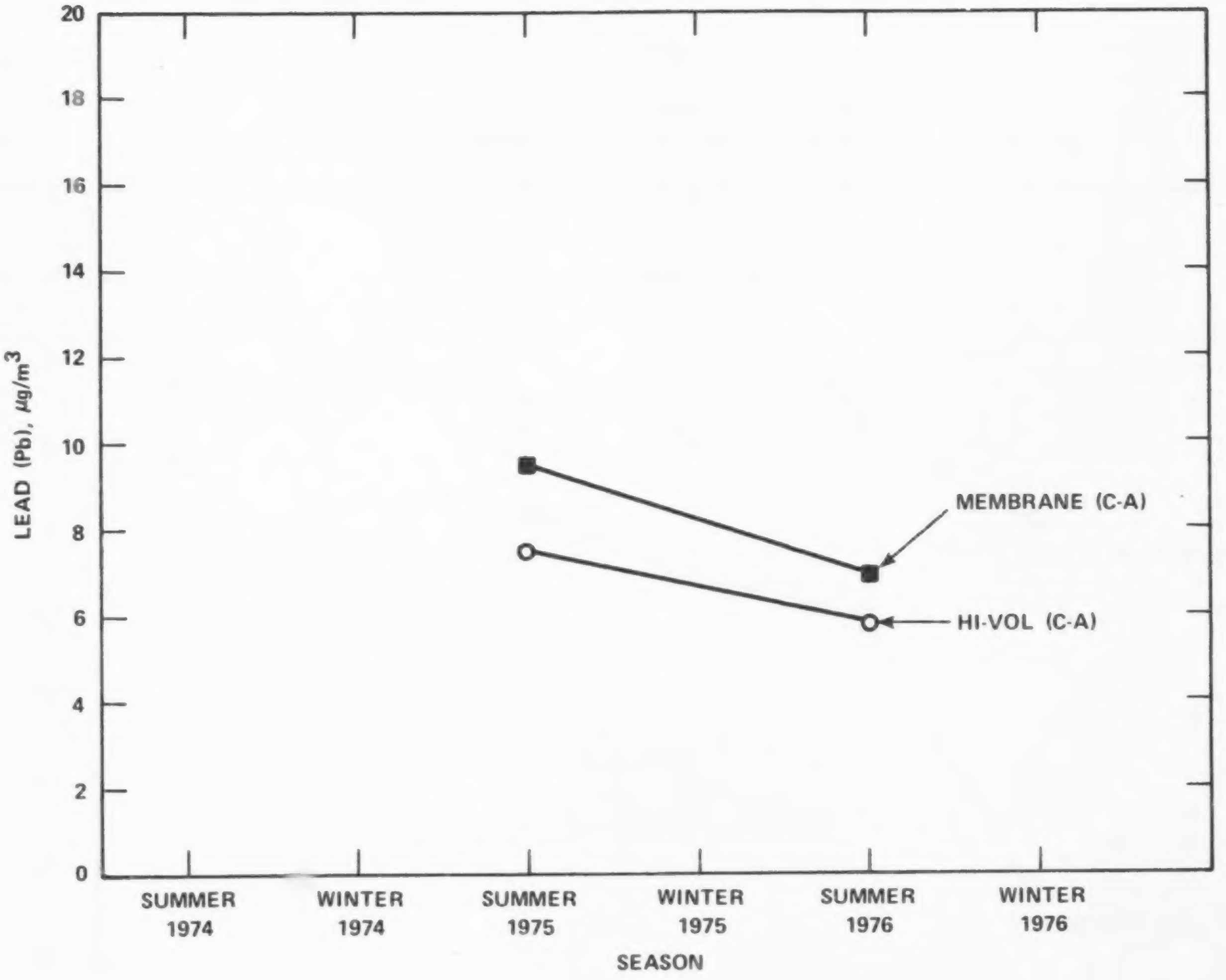


Figure 17. 1500-1900 hr freeway contribution of Pb (summer seasons only).

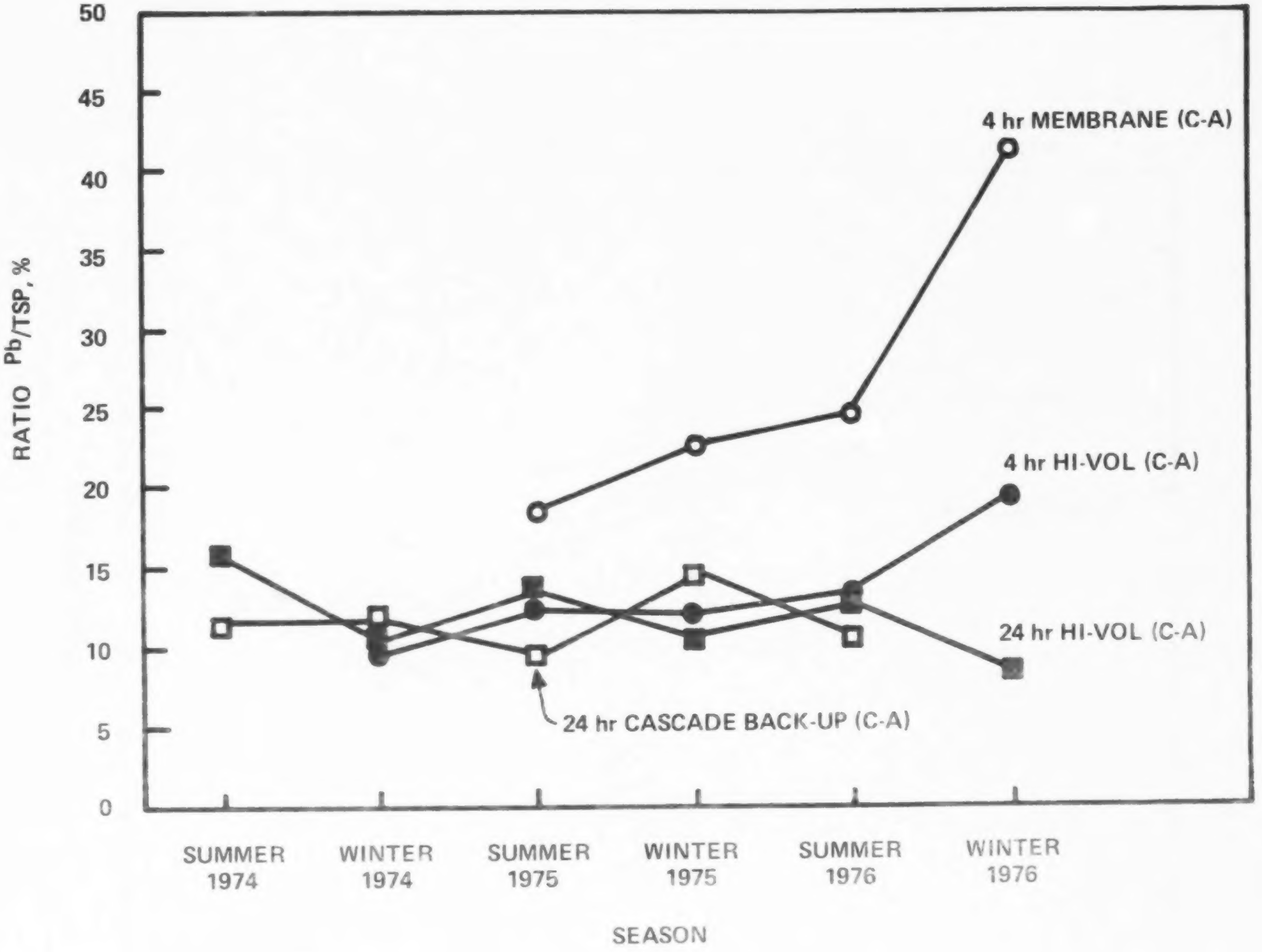


Figure 18. Pb as fraction of TSP (freeway contribution).

shows that the hi-vol and the cascade back-up samples have shown essentially no change in the ratio of Pb to TSP since 1974. The disagreement of the 4-hour membrane reflects the poorer precision (factor of 3) of the 4-hour membrane in measuring TSP as compared to the other methods. The consensus of methods in Figure 18 is that both TSP and Pb have apparently decreased. This interrelationship will be examined in greater detail later in this paper.

The spatial distribution of "Summer" season Pb is shown in Figure 19. Unlike TSP, Pb is very strongly influenced by sampling interval because of meteorology and the relatively low background levels. Site B is significantly higher than Site A, even on a 4-hour basis. An unexpected observation is that the average downwind Pb level at Site C is essentially the same for both the 4-hour and the 24-hour bases. The C minus A differences are greater for the 4-hour interval because of the low background levels. The decrease of Pb from Site C to Site D is greater on a 24-hour basis because of less favorable meteorology.

Comparison of the spatial distribution of 4-hour TSP and Pb in Figure 20 clearly shows the large TSP background as compared to the small Pb background. Note that TSP decreases more rapidly from Site C to Site D than does lead. This is probably due to the more rapid dilution of the fine particle lead and fallout of large particle lead. Because of the very small mass median diameter of Pb particles, they apparently behave much like a gas, and consequently correlate extremely well with measurements of carbon monoxide at Sites A and C.

The relation of lead and bromine should be well defined, since the principal lead emission from non-catalyst vehicles is lead bromochloride (PbBrCl). Figure 21 shows that the two measurements correlate very well (coefficient of 0.99) and have a mass ratio of lead to bromine of 2.3, which is approximately stoichiometric.

SULFATE DATA

Sulfate ($SO_4^=$) measurements are the most important analyses performed on LACS aerosol samples. Since a reliable ambient sulfuric acid aerosol sampler is not available, the measurement of water soluable sulfates provides a gross indication of the sulfur emissions as sulfates or sulfuric acid from the automobile. Based on the very low sulfate emission rates of non-catalyst cars, it was expected that during the first year after introduction of the catalyst, the freeway sulfate contributions would be small. This small difference ($<0.5\ \mu g/m^3$) unfortunately was overlaid on a background sulfate level as shown in Figure 22 that was much higher than expected. This plot shows that the initial sulfate levels by hi-vol and membrane were in the range of 12 to 16 $\mu g/m^3$, especially during the "Summer" seasons. The seasonal changes in sulfate are not due to freeway influence, but increases in the sulfate levels in the summer are due primarily to increased photochemical activity in the LA basin. Examination of the "Summer" season background in Figure 23 shows a substantial decrease in background sulfates as a consensus by all methods. This decrease from 1974 to 1976 of approximately 25% is probably not related to automotive emissions, since these constitute only a

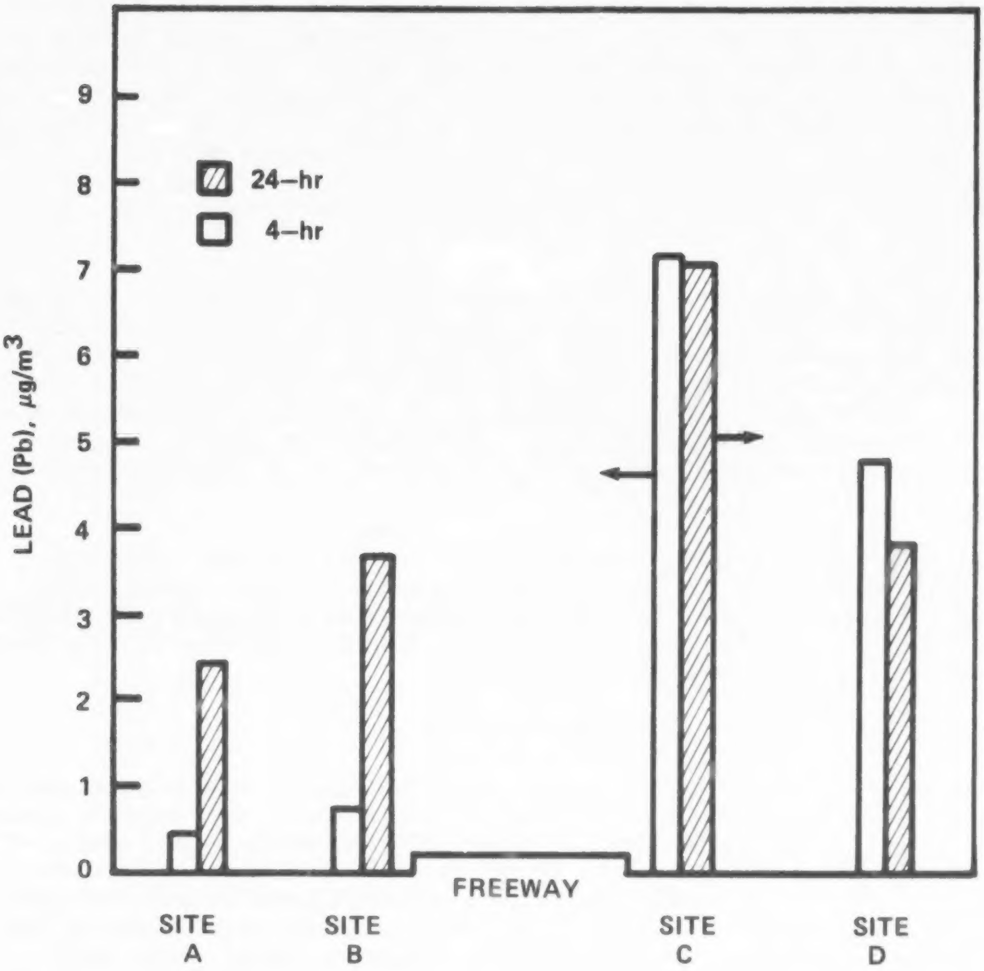


Figure 19. Spatial distribution of lead by sampling interval (summer seasons).

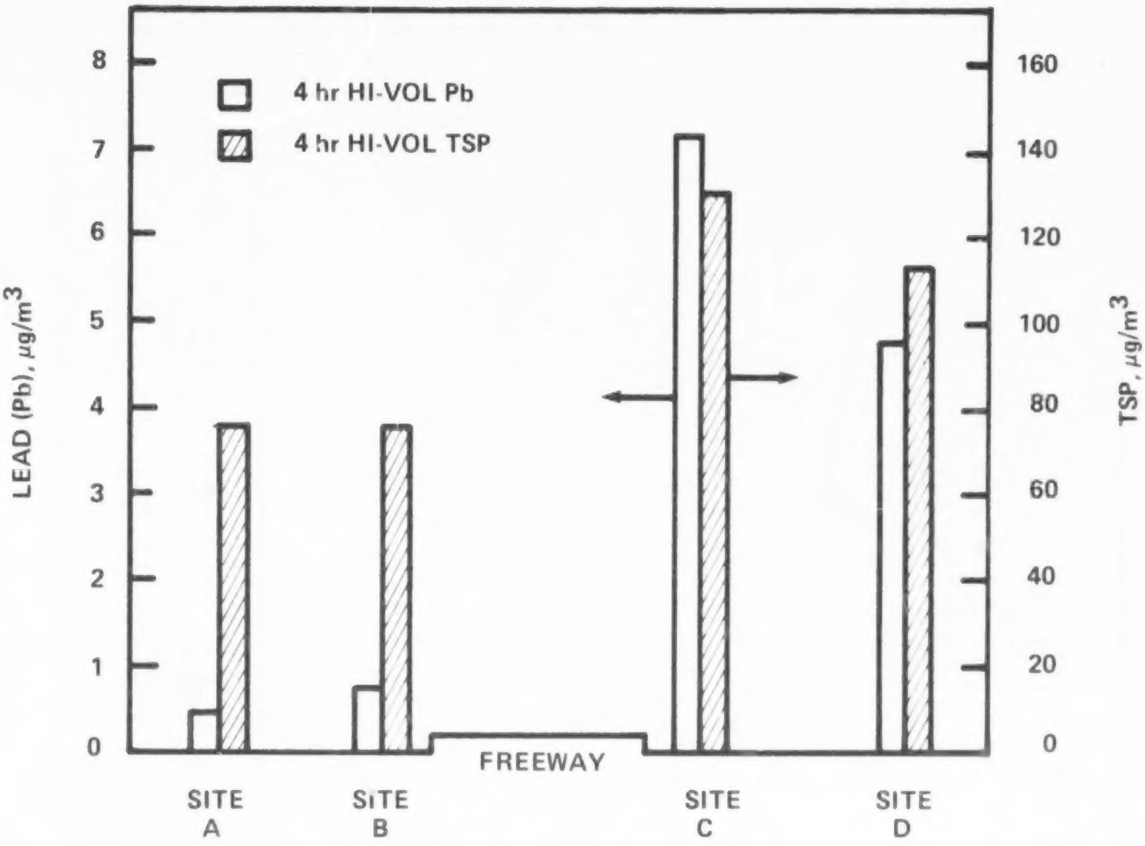


Figure 20. Spatial distribution of 1500-1900 hr TSP and lead (summer seasons).

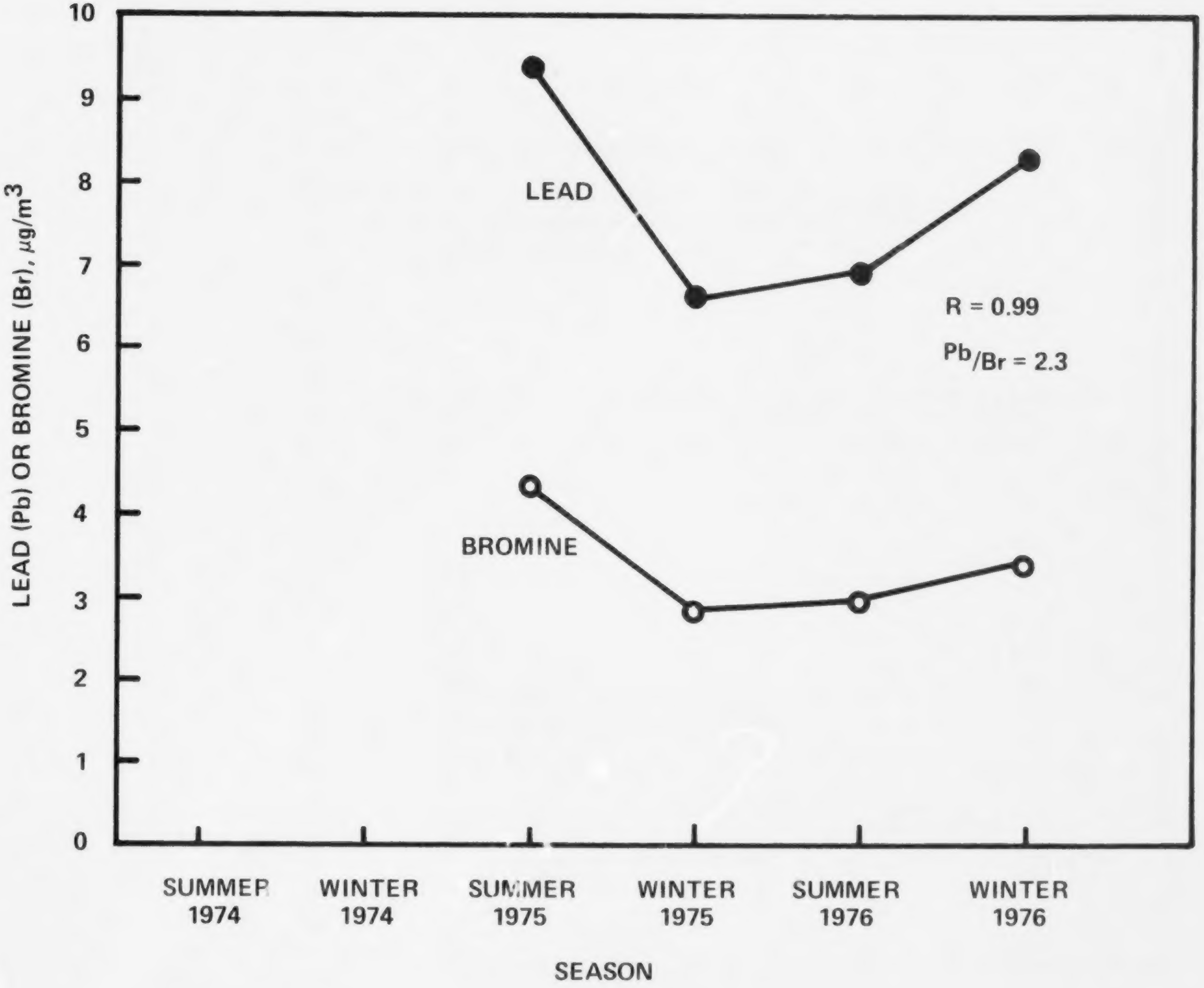


Figure 21. 1500-1900 hr freeway contributions of lead and bromine.

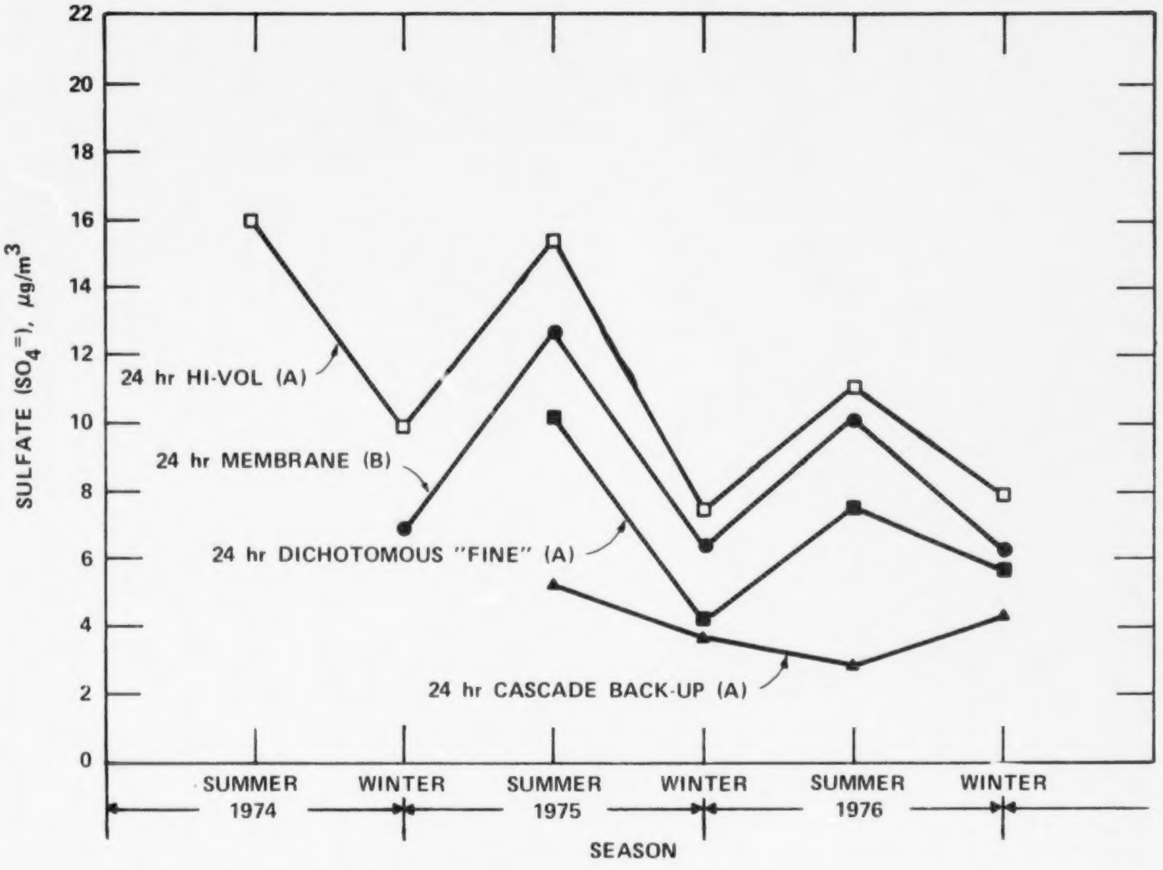


Figure 22. Background sulfate trends.

very small fraction of the total sulfur emitted daily into the ambient air in Los Angeles. The proportions of sulfate collected by the various types of samplers compared to the sizes of the aerosol fractions are consistent with the distribution of $SO_4^=$ by size collected by the Andersen sampler. In general the higher sulfate values for the hi-vol as compared to the membrane suggest the possibility of artifact sulfate formation from SO_2 conversion, however, the previous agreements for TSP and Pb between these various types of samplers have also been less than ideal.

The dashed line in Figure 23 represents sulfate data obtained from the Southern California Air Pollution Control District at a site located less than a mile from the LACS sites. These data using a 24-hour hi-vol agree very well with our hi-vol background data. Comparison in Figure 24 of the monthly sulfate data from the two monitoring programs indicates the very favorable comparison, even with the expected spatial differences in sulfate levels.

The size distribution of sulfate particles on a 24-hour summer season basis is shown in Figure 25. These plots again show that TSP sulfate is not log-normally distributed, and the size distribution upwind and downwind is essentially the same. It is interesting to note, however, contrary to the originally assumption that the sulfate would be found only in very small particles, there is a significant fraction greater than 1.0 micron. According to the plots approximately 30% is greater than 1.0 micron and 2% greater than 2.5 microns.

The freeway contribution of sulfate on a 24-hour basis as measured by a variety of samplers is shown in Figure 26. Notice that only by expanding the sulfate scale can the consensus difference of approximately 0.5 $\mu g/m^3$ in the summer of 1976 be demonstrated. Because the C minus A differences showed such a small contribution from the freeway, the difference in hi-vols between Sites D and B was also computed (even though B is not a true background) to examine the negative sulfate differences in 1975. The "Summer" season averages shown in Figure 27 indicate that even though the dichotomous "Fine" fraction and cascade back-up sulfate differences were positive, the freeway contribution of both sets of hi-vols was inexplicably negative in the "Summer" of 1975.

The previous sulfate contribution data presented in the LACS semi-annual reports were based only on hi-vol measurements. The 4-hour freeway contribution of sulfate shown in Figure 28 not only gives the hi-vol results but adds the 4-hour membrane differences. This graph shows a substantial difference in both absolute level and trend between the two methods. Whereas the 4-hour hi-vol has indicated as much as 5.2 $\mu g/m^3$ sulfate contribution of sulfate, the 4-hour membrane is averaging only 1.0 $\mu g/m^3$. The summer season plot in Figure 29 also shows the nearly four-fold difference between the hi-vol and membrane results. Again the problem of artifact formation on glass fiber substrates, appears to be relevant. The ratios of $SO_4^=$ to TSP for several data sets are shown in Figure 30. These plots dramatically indicate that the proportion of sulfate collected on the 4-hour hi-vols is significantly greater than the other methods, suggesting artifact sulfate formed by conversion of sulfur dioxide. However, the fraction of artifact sulfate formed in the 24-hour hi-vol appears to be an insignificant portion of the total.

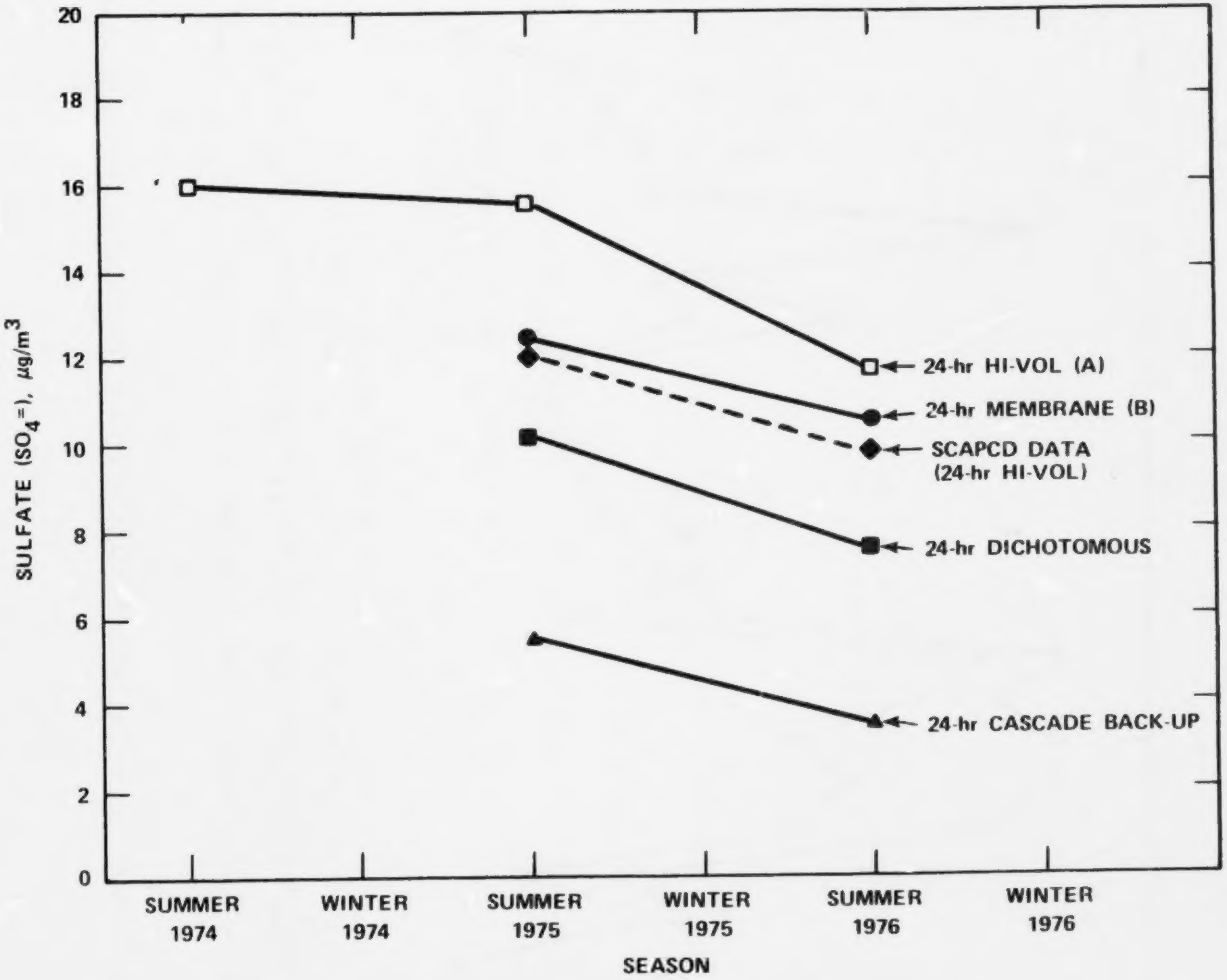


Figure 23. Background sultate trends (summer seasons only).

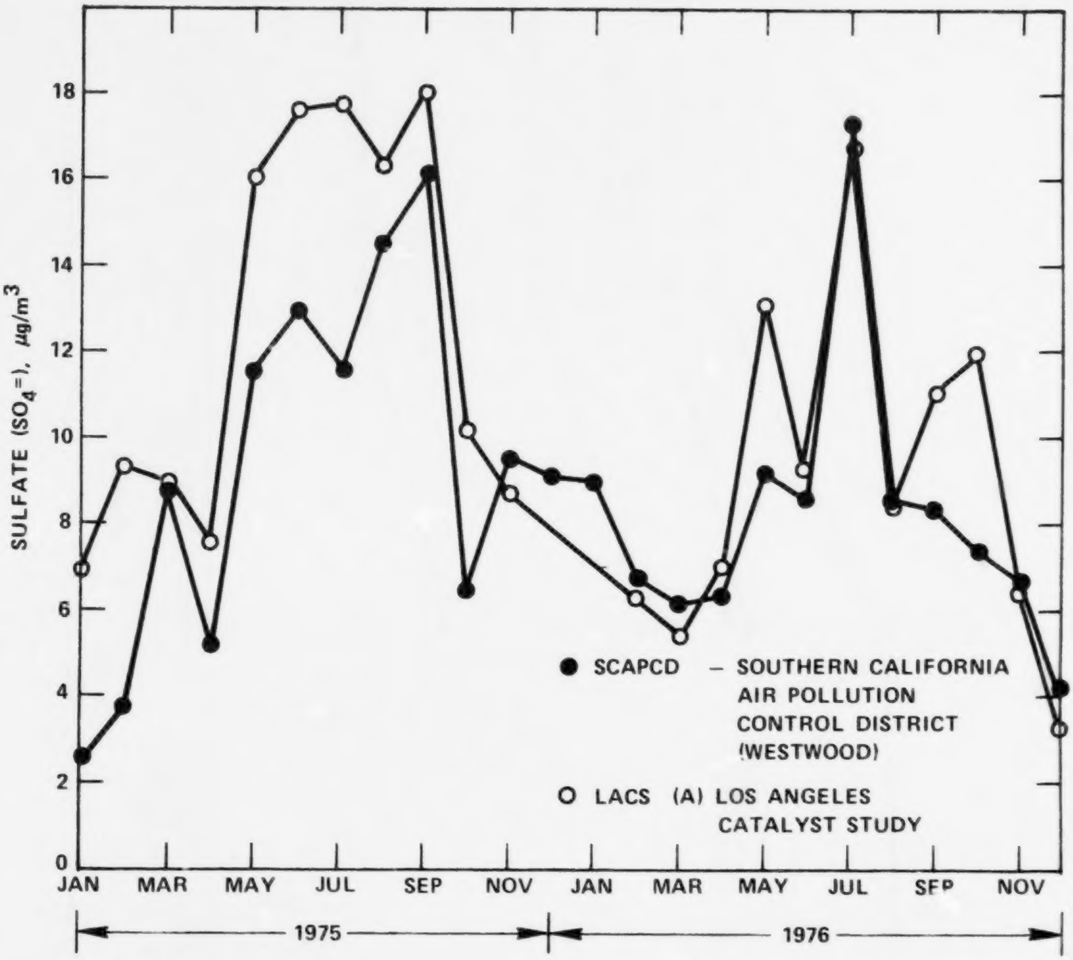


Figure 24. Comparison of background sulfate data - LACS/SCAPCD (24-hr hi-vols).

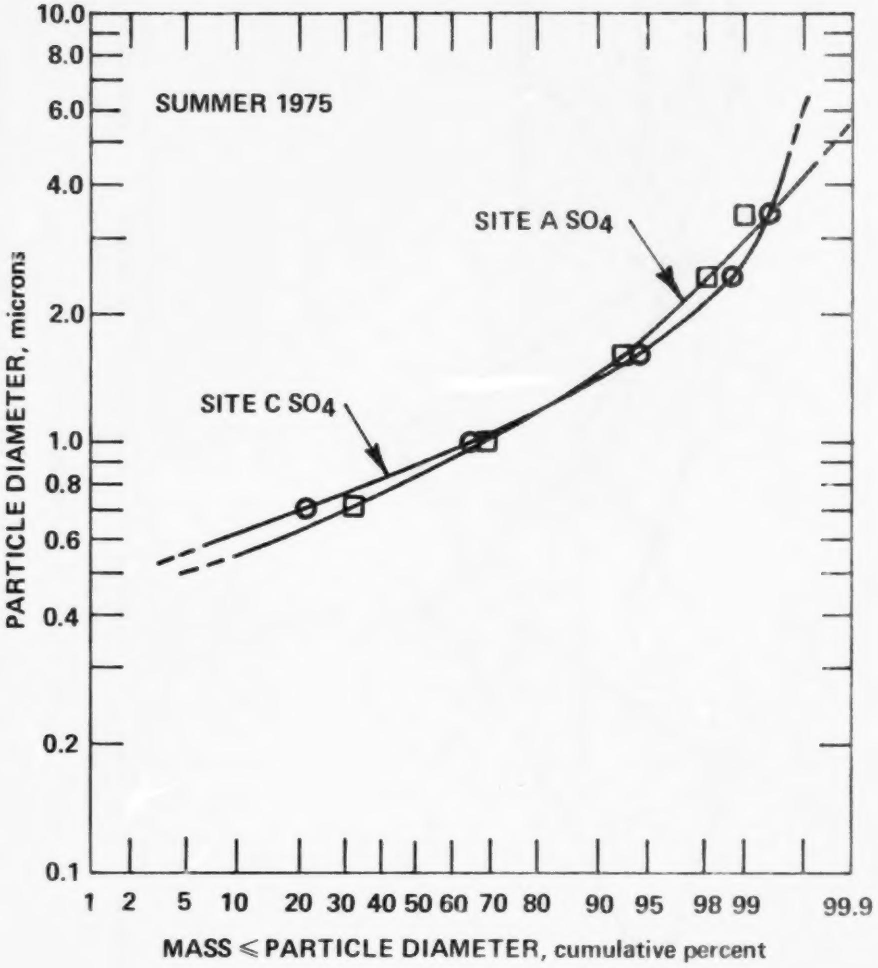


Figure 25. Twenty-four hour cascade composites - $SO_4^=$.

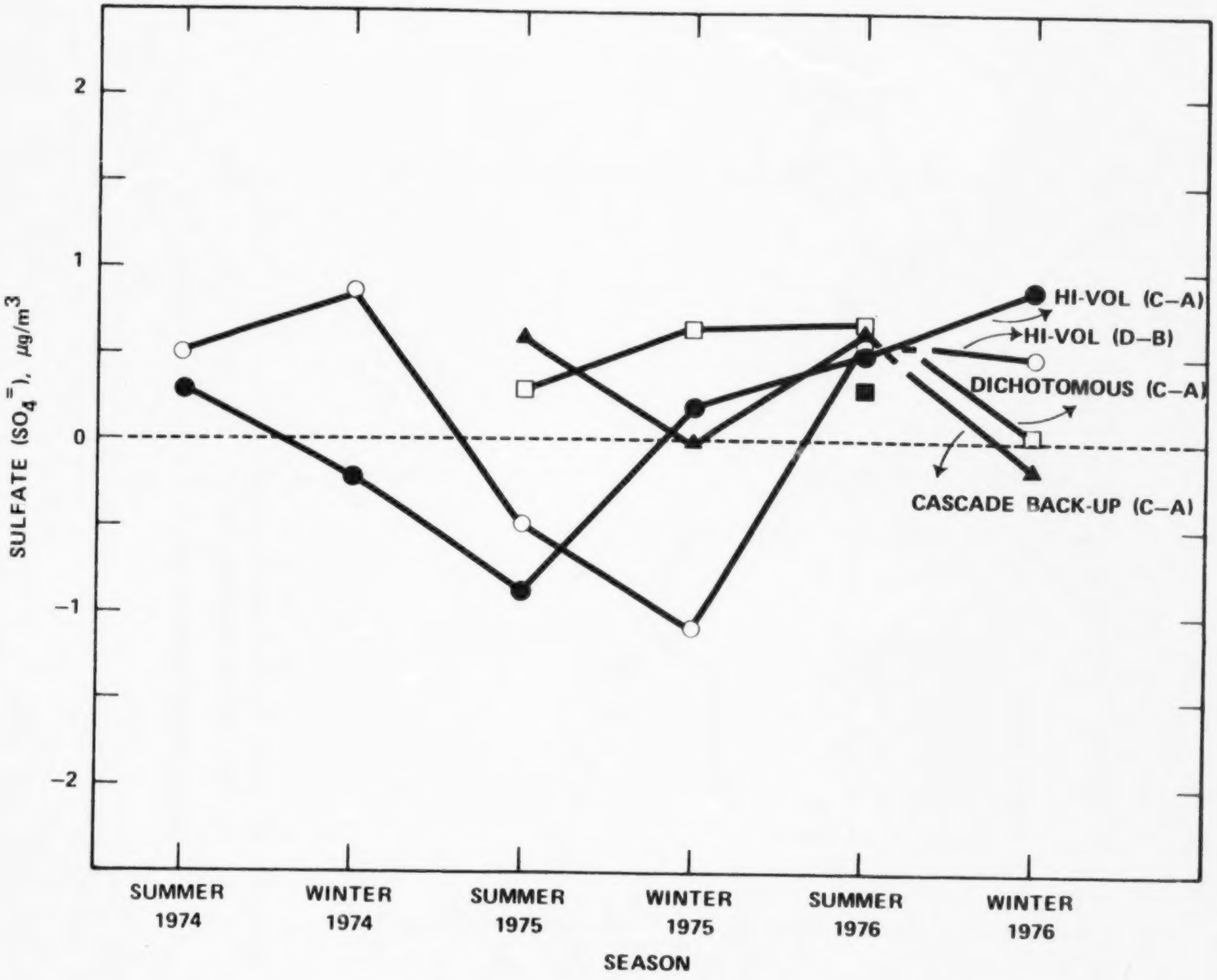


Figure 26. Twenty-four hour freeway contribution of sulfate.

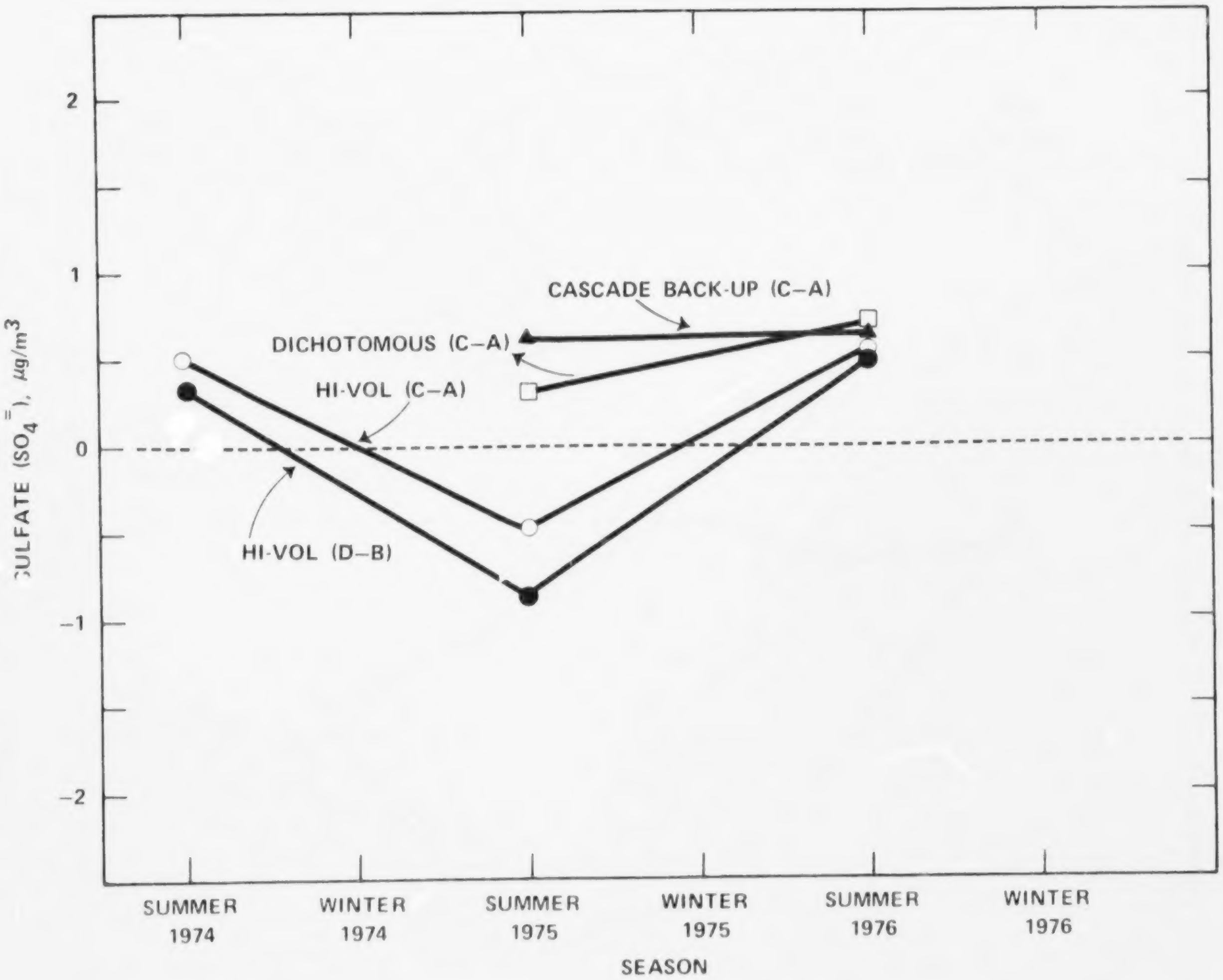


Figure 27. Twenty-four hour freeway contribution of sulfate (summer seasons only).

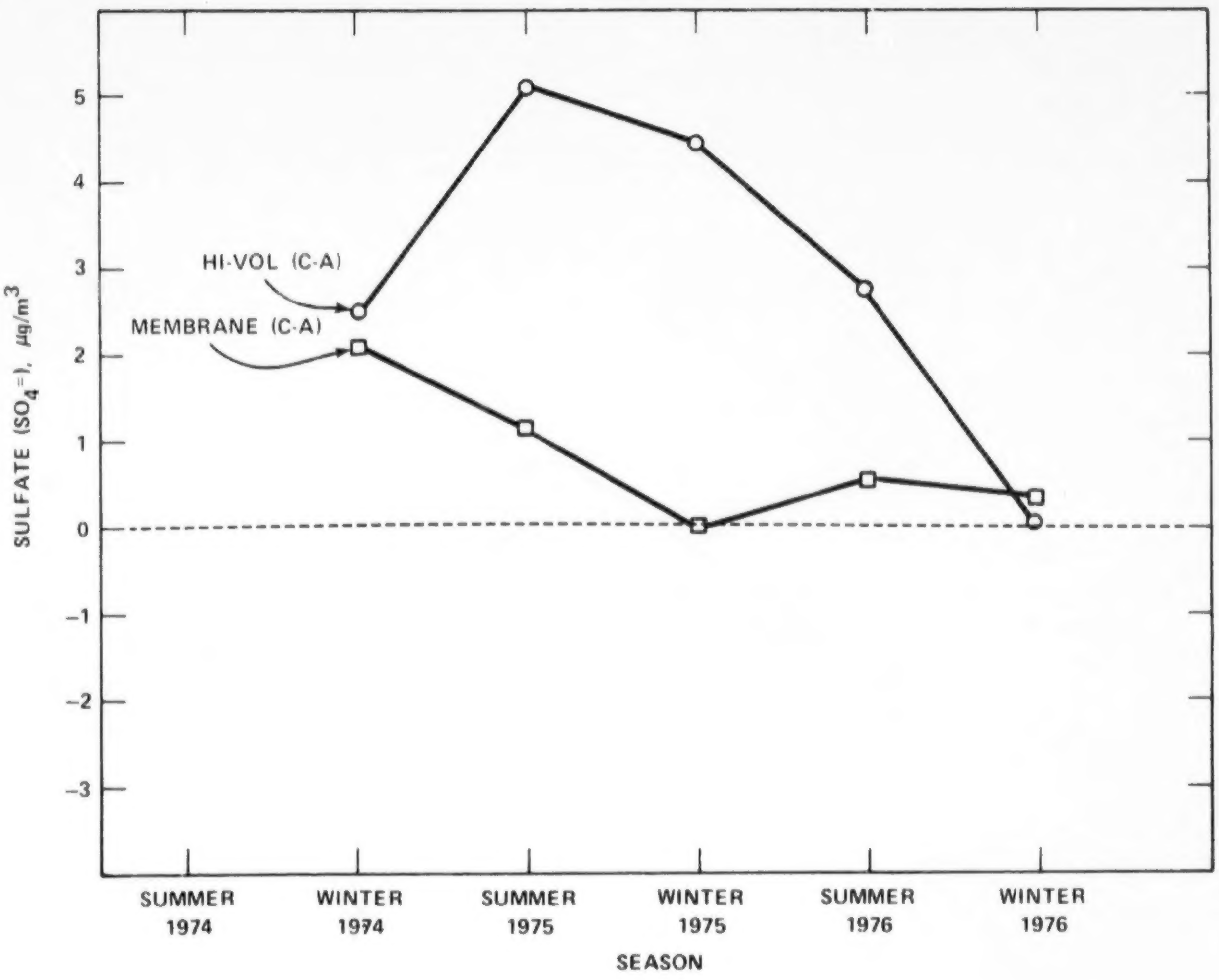


Figure 28. 1500-1900 hr freeway contribution of sulfate.

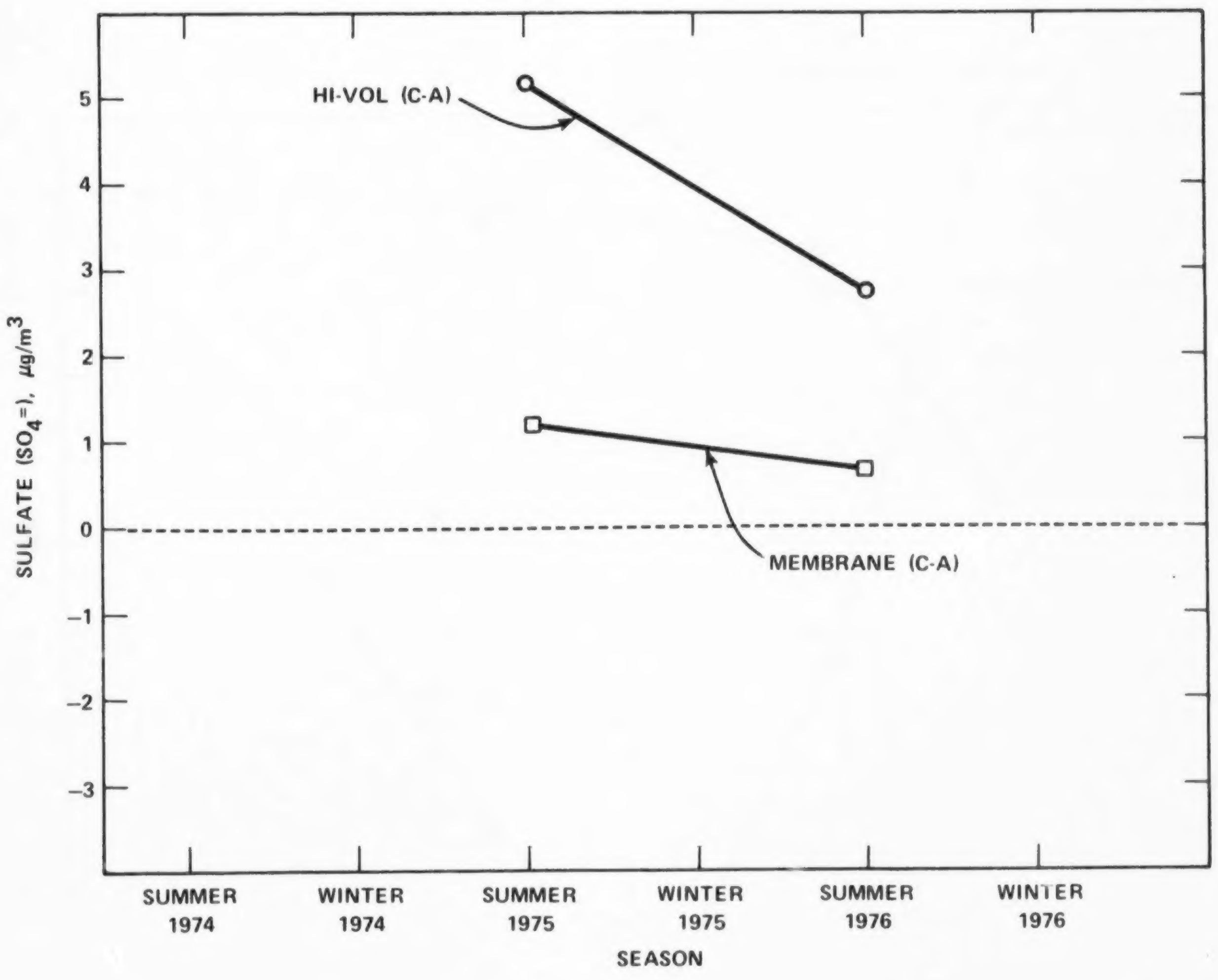


Figure 29. 1500-1900 hr freeway contribution of sulfate (summer seasons only).

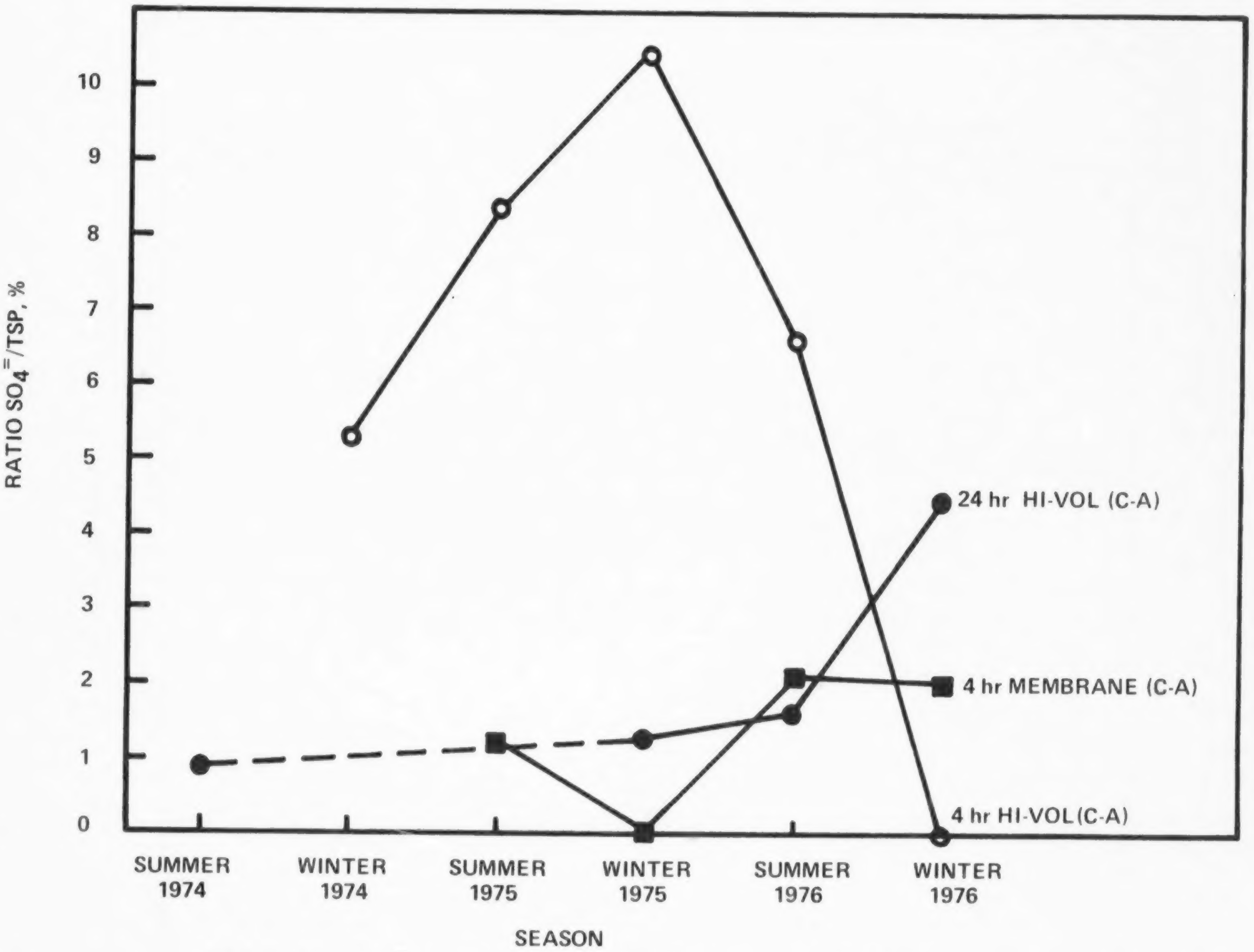


Figure 30. $SO_4^=$ as fraction of TSP (freeway contribution).

The sulfur contents of gasolines in the Southern California area since 1974 are shown in Figure 31 where the average weight percent sulfur in leaded and unleaded regular gasolines is weighted by consumption. Unleaded gasoline contains approximately one-half the sulfur of the leaded gasoline. Also, it is apparent that there has been no significant increase or decrease in the sulfur contents since 1974. Since the majority of sulfur in gasoline is emitted as sulfur dioxide from automobiles, the freeway contribution of SO_2 is shown in Figure 32. This graph shows a seasonal pattern because of meteorology, even though sulfur in the fuel is not seasonal. Overall there appears to be a slight decrease in SO_2 from 1974 to 1976, if only the summer seasons SO_2 values are considered. Comparison of the 24-hour SO_2 and $SO_4^=$ levels obtained from Site A plotted in Figure 33 shows the freeway influence on SO_2, and the seasonal change in $SO_4^=$ resulting from the increased photochemical conversion of SO_2 to $SO_4^=$ in the "Summers."

To further examine the discrepancy between the 4-hour hi-vol and the other methods for sulfate, led to comparison with other parameters such as SO_2, total sulfur, temperature, and relative humidity. The only parameter which so far shows a significant correlation is relative humidity. Figure 34 shows the hi-vol C minus A $SO_4^=$ difference and the background 4-hour hi-vol $SO_4^=$ as compared with the relative humidity as measured at Site A. The peak in the summer of 1975 and subsequent decline of all three measurements tends to support the contentions in the literature that humidity is an important factor. In order for the sulfate difference measurements to be affected by artifact formation, there must be a difference in conditions at the two sites. There is certainly more SO_2 at Site C than at Site A, however preliminary comparisons show little correlation of the measured sulfate contribution with the SO_2 level. Because automobiles emit water vapor and heat, there could be a slight increase in relative humidity and temperature downwind, and measurements to quantify these expectations are being made.

One problem area which became apparent from examining freeway $SO_4^=$ contribution information is shown in Figure 35. Comparison of $SO_4^=$ by the Methyl Thymol Blue (MTB) method to sulfate from XRF sulfur measurements was very good (correlation coefficient = 0.92) for cellulose ester membrane filters, and no problem was foreseen with the Teflon dichotomous filters. As can be seen the two methods agree in Figure 35 within 1.0 $\mu g/m^3$, but do not indicate the same trend in freeway contribution. Since each of the points represents an average of many analyses, it is felt that the difference is real.

Because X-ray Fluorescence is a surface measurement technique as compared to the MTB method which extracts the entire filter, one could expect XRF measurements to be slightly lower if there was a significant amount of material embedded in the filter. In this case, however, the XRF differences are greater and this rationale apparently does not apply. The most probable explanation is that the MTB method is not as sensitive as XRF in this range ($<$ 1.0 $\mu g/m^3$).

RELATED DATA

Because the most prevalent sulfate compounds in the ambient air are probably ammonium salts, aerosol samples are also analyzed for ammonium ion

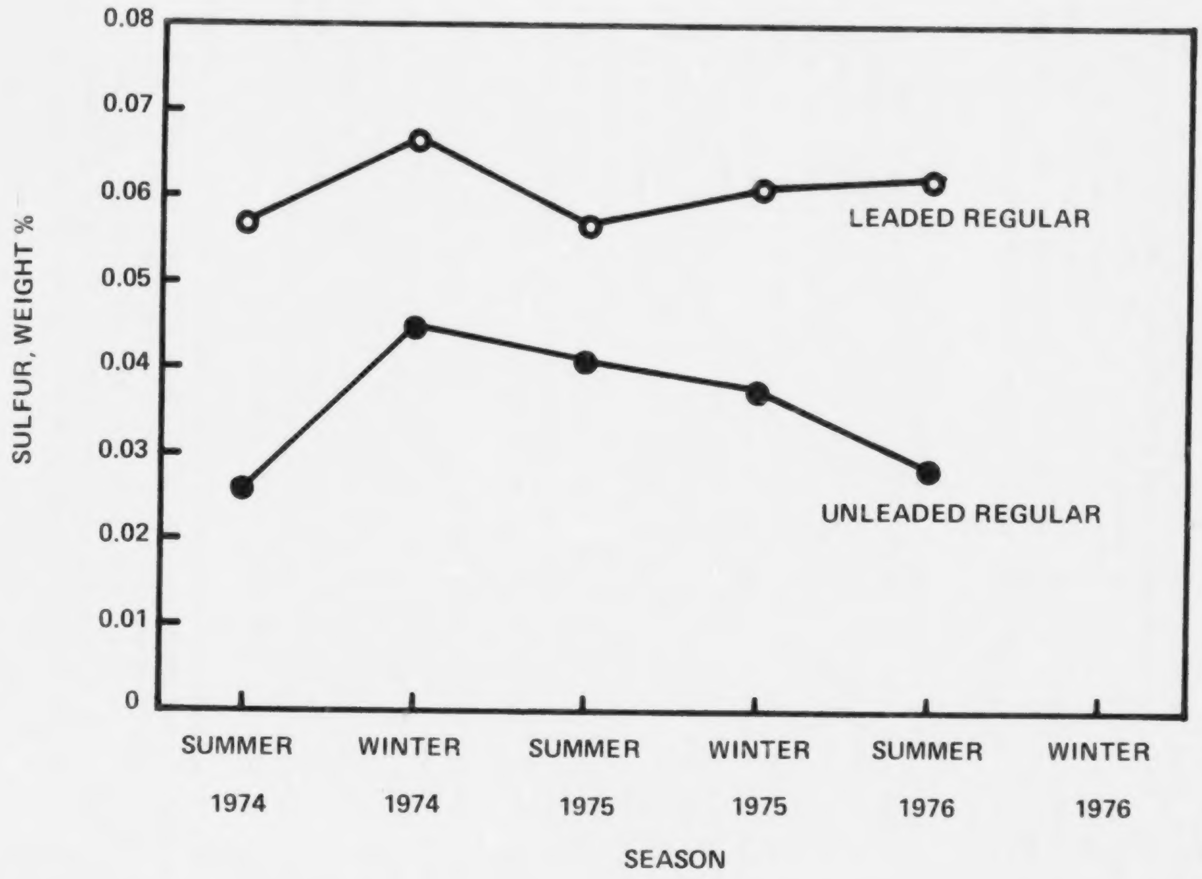


Figure 31. Sulfur content of gasoline in Southern California (major brands weighted by consumption)

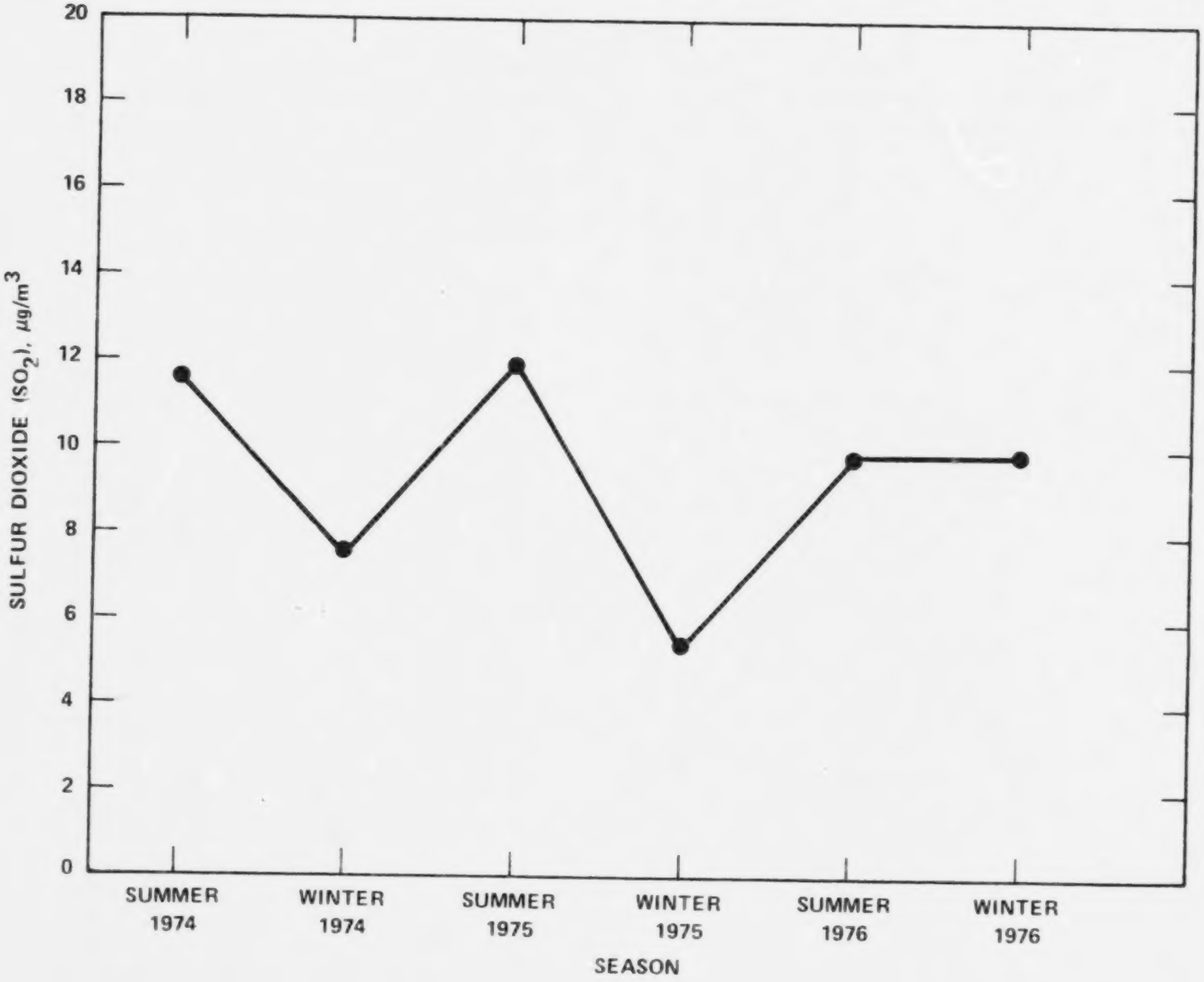


Figure 32. Twenty-four hour freeway contribution of sulfur dioxide.

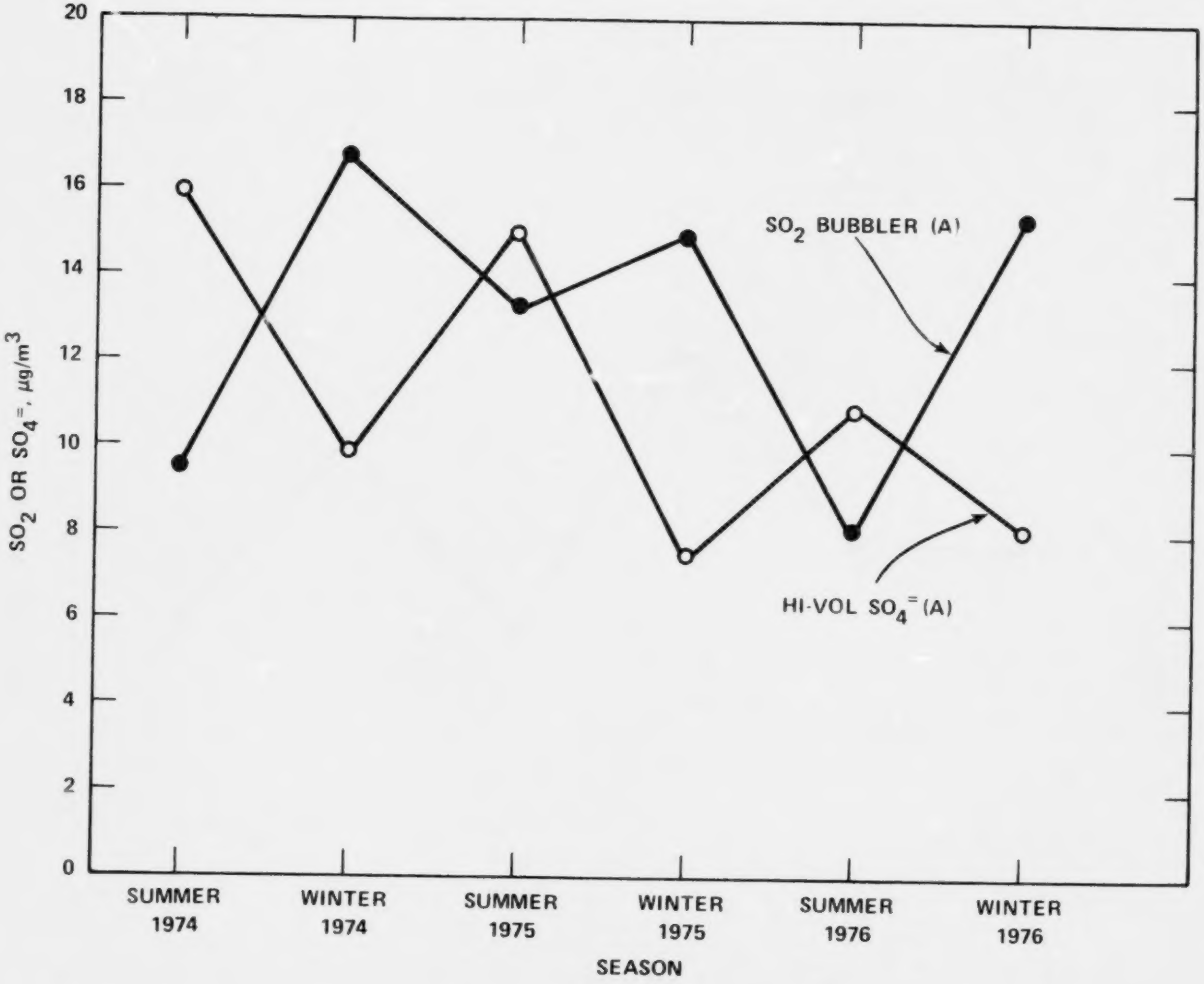


Figure 33. Comparison of 24-hr SO_2 and hi-vol $SO_4^=$.

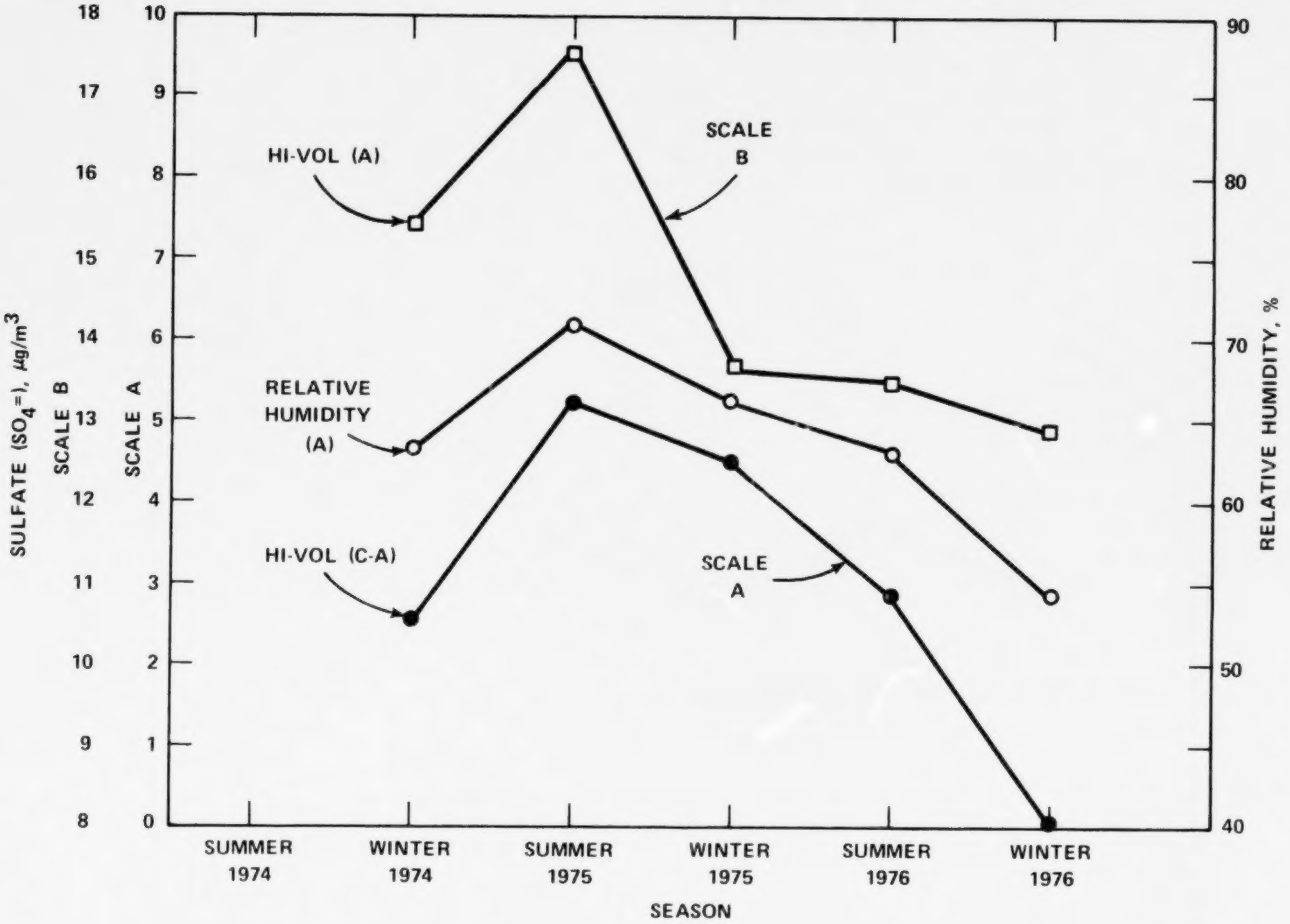


Figure 34. Relation of 4-hr hi-vol sulfate to relative humidity.

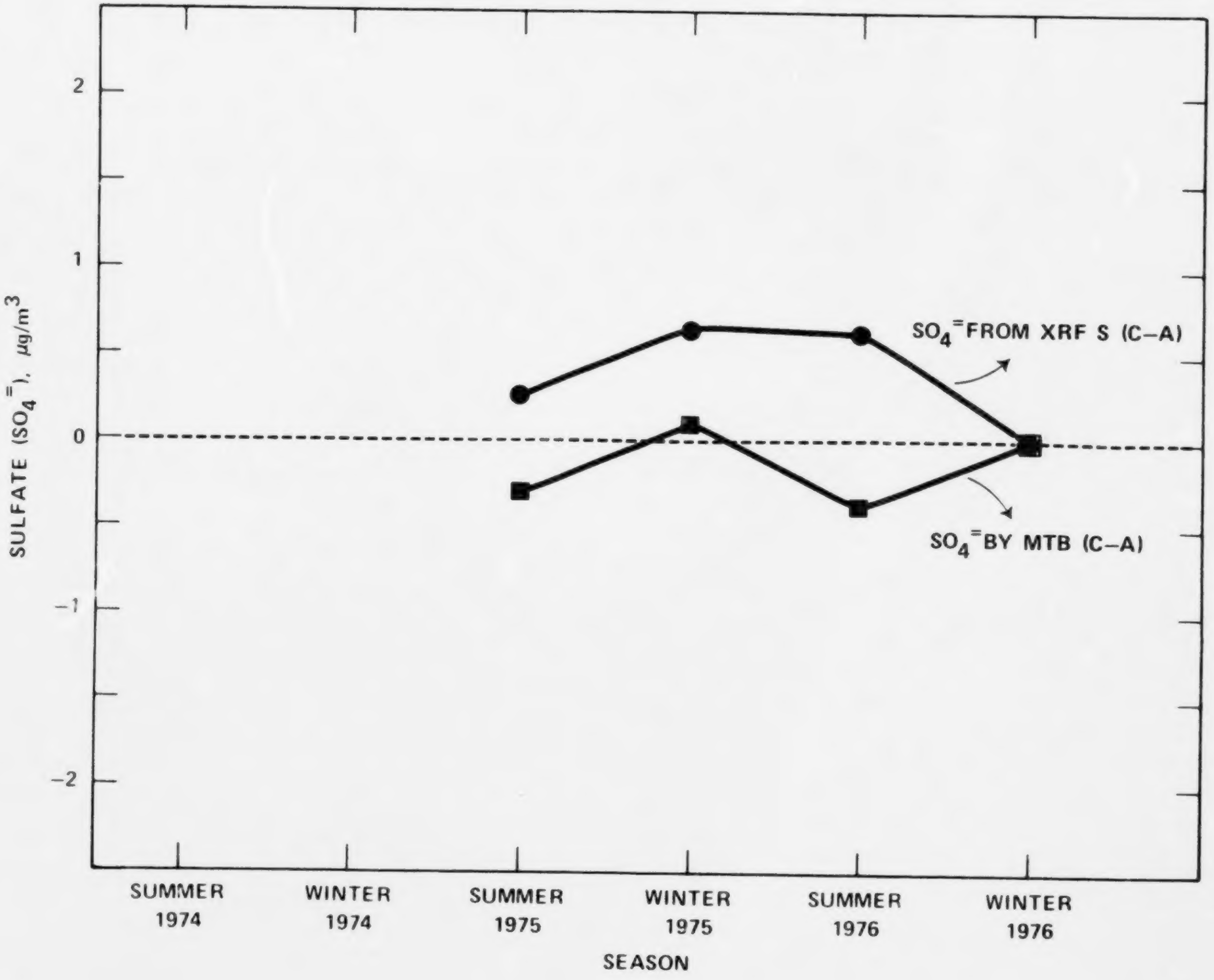


Figure 35. Freeway contribution of sulfate - dichotomous samples.

(NH_4^+). The data in Figure 36 shows that both the hi-vol and membrane exhibit a small freeway contribution of NH_4^+, even though the trends do not agree in the summer of 1976, and the measured hi-vol NH_4^+ levels are known to be erroneously low because of sample degradation. The size distributions of NH_4^+ at both sites are shown in Figure 37, and indicate that like $SO_4^=$ there is little difference between sites and the relations are not log-normal. If the sulfate and ammonium distributions for each site are plotted together as in Figures 38 and 39, it is obvious that below 1.0 micron the two species are in the same size fraction. Above this size they apparently are not related to one another, but must be combined with other anions and cations. This would also be true for as much as 20% of th aerosol collected by the less than 2.5 micron dichotomous "Fine" fraction, but none on the cascade back-up filters.

Nitrate (NO_3^-) analyses have been performed on aerosol samples in all size ranges, but there appears to be no significant contribution of nitrate from the freeway. The size distribution of NO_3^- in Figure 40, however, suggests that there is a difference in aerosol size across the freeway. There appears to be agglomeration of NO_3^- particles across the freeway, perhaps due to reaction with emission products.

In 1975 dustfall buckets, which were added at all sites collect non-suspended (settleable) particulates greater than 100 microns. Compositing the summer season results for mass in Figure 41 shows the comparison with hi-vol TSP. Both show an increase across the freeway, although dustfall is more severely influenced by proximity to the freeway than is the hi-vol. Note also that the dustfall drops off from Site C to Site D faster than does the TSP. Analysis of the dustfall samples for Pb gave the interesting conclusion shown in Figure 42 that hi-vol Pb correlates spatially very well with dustfall lead near a freeway. This relation may be useful in providing estimations of total ambient lead burdens.

DISCUSSION

It is apparent from the data presented in this report that use of the catalyst is reducing emissions to the ambient air. The freeway contributions of TSP and Pb have both decreased since the beginning of the study. The nearly constant ratio of Pb to TSP since the beginning of the study was puzzling until the information shown in Table IV was obtained from Dr. Ronald Bradow of the Mobile Sources Emissions Research Branch (EPA). These numbers represent typical emission rates from catalyst and non-catalyst cars operated in driving cycles similar to Los Angeles Freeway conditions. For a non-catalyst equipped (pre-1975) vehicle, the typical Pb emission rate of 40 mg/mi is 50% of the total mass emitted. The balance of the emissions are primarily carbonaceous materials and fuel additives such as bromine. By contrast the 20 mg/mi emissions from a catalyst equipped auto consist almost entirely of a sulfuric acid aerosol in equilibrium with water. The carbonaceous aerosol material of the non-catalyst auto is converted to gaseous forms, by the catalyst, and Pb and its related additives are omitted from the fuel. Assuming the catalyst to total vehicle mix based on estimated vehicle miles travelled is 30%, the estimated mass emission rate would be 62 mg/mi compared to a lead emission rate of 28 mg/mi, resulting in a ratio of Pb/mass of 45%. This number is not

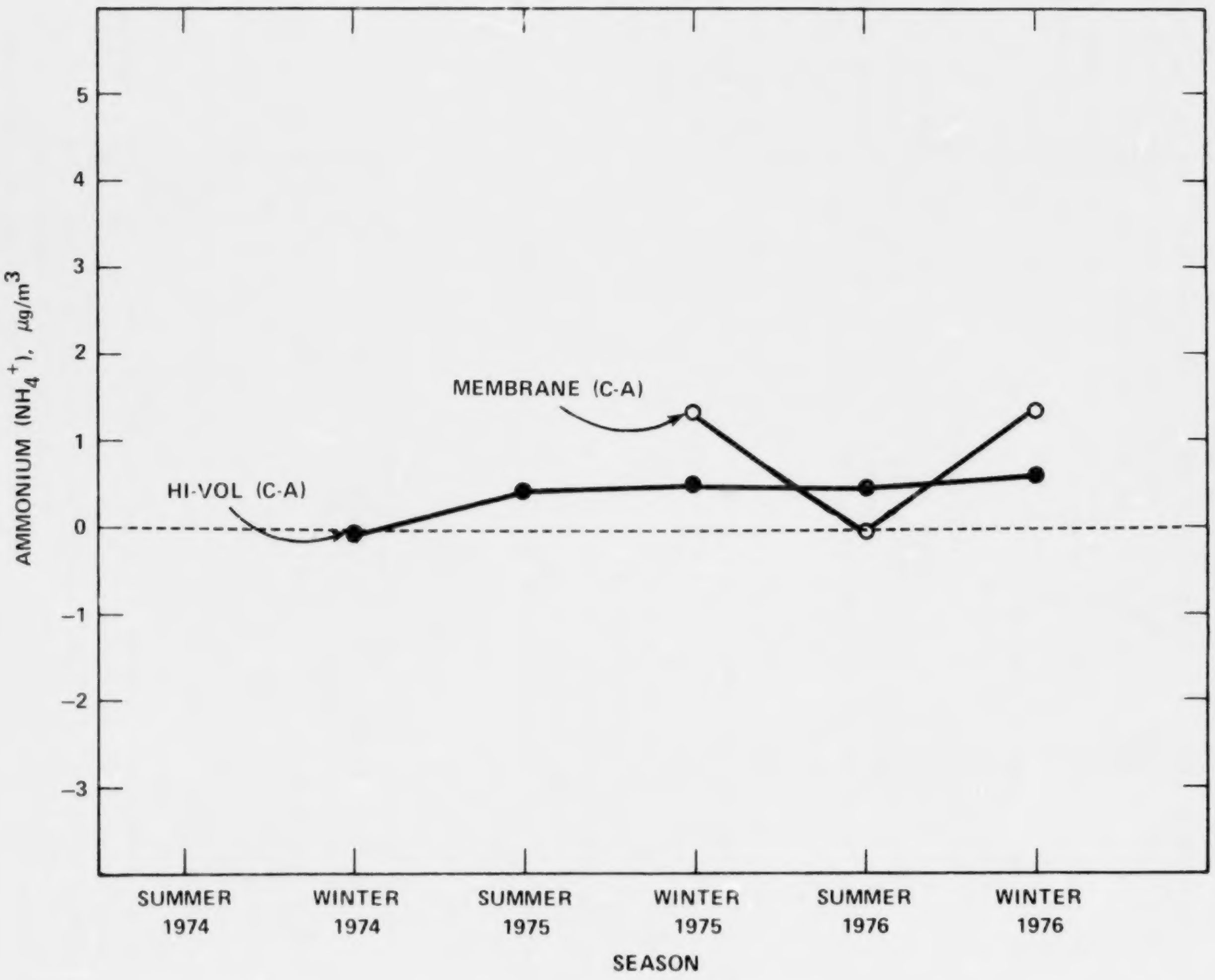


Figure 36. 1500-1900 hr freeway contribution of ammonium.

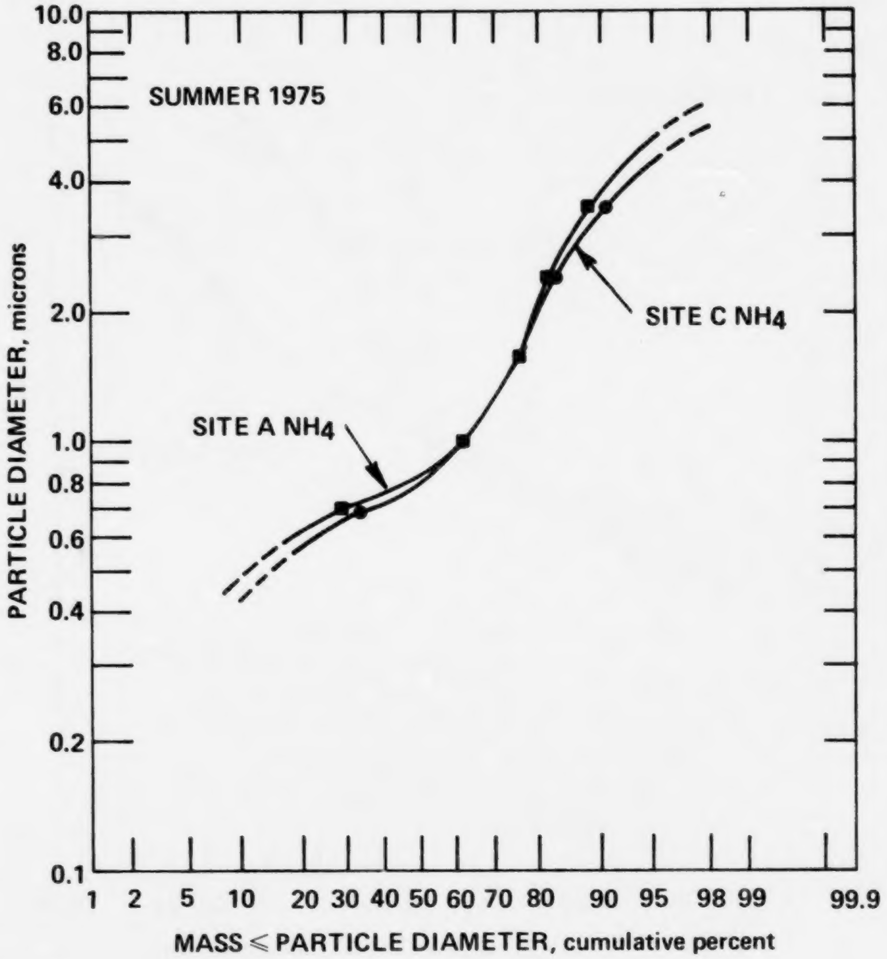


Figure 37. Twenty-four hour cascade composites - NH_4^+.

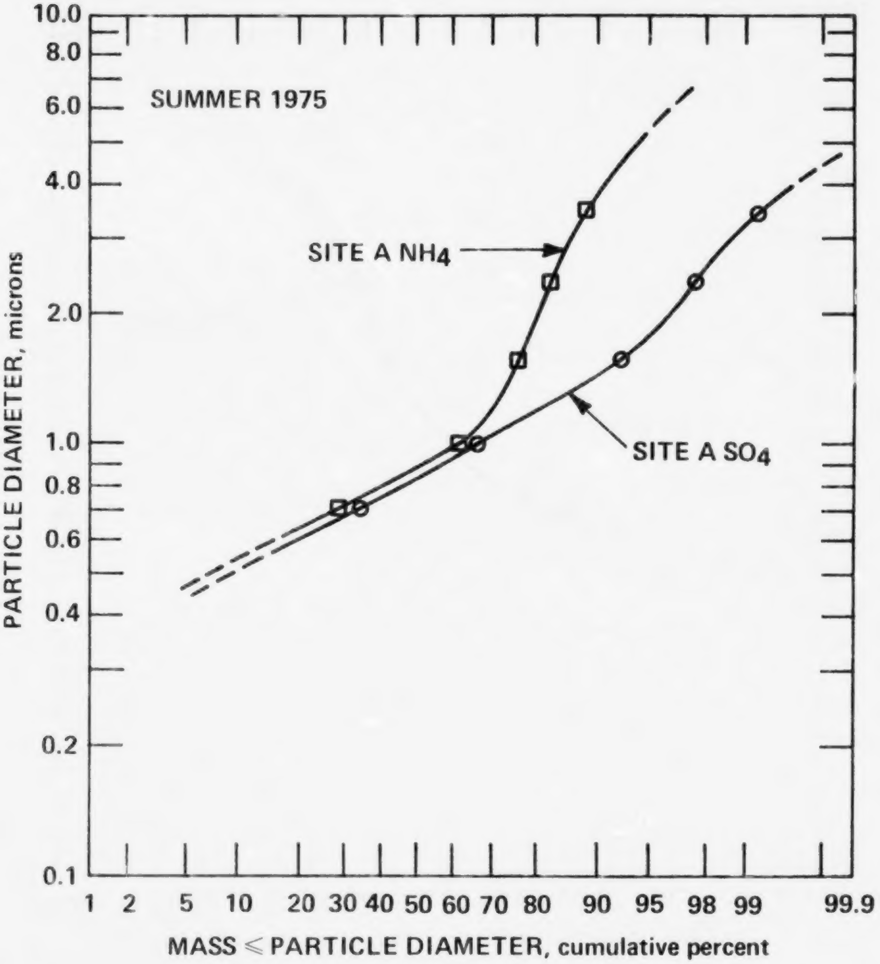


Figure 38. Twenty-four hour cascade composites - $NH_4^+/SO_4^=$ upwind.

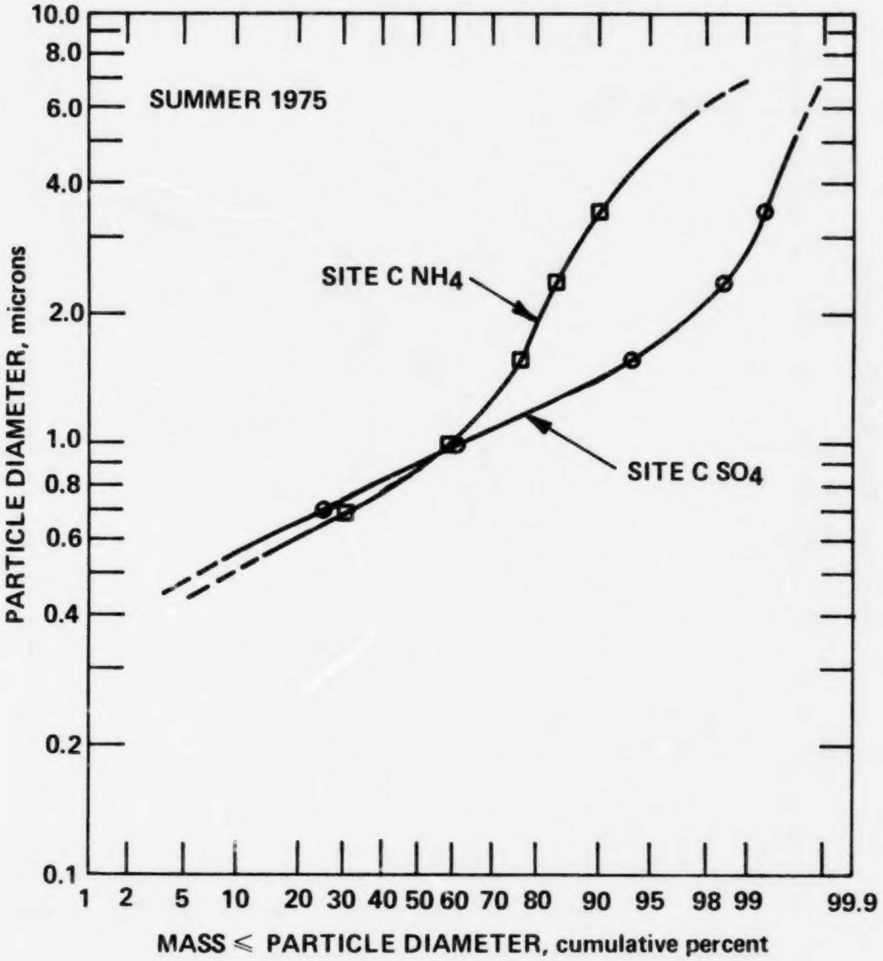


Figure 39. Twenty-four hour cascade composites - $NH_4^+/SO_4^=$ downwind.

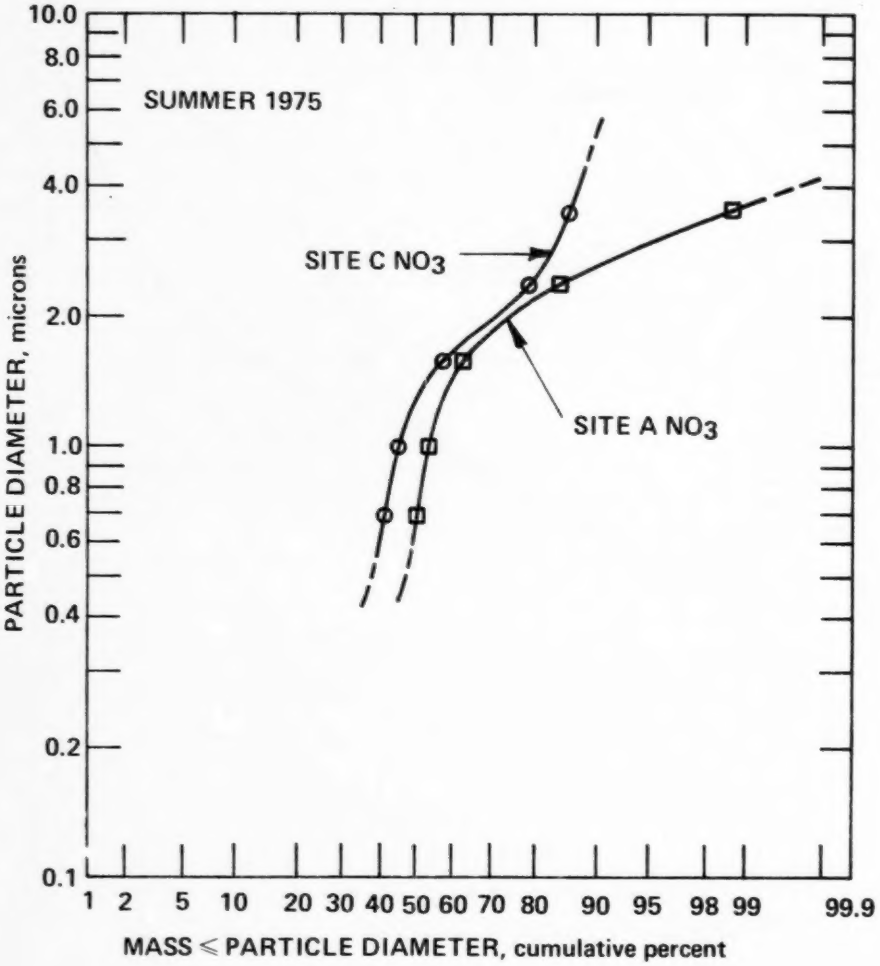


Figure 40. Twenty-four hour cascade composites - NO_3^-.

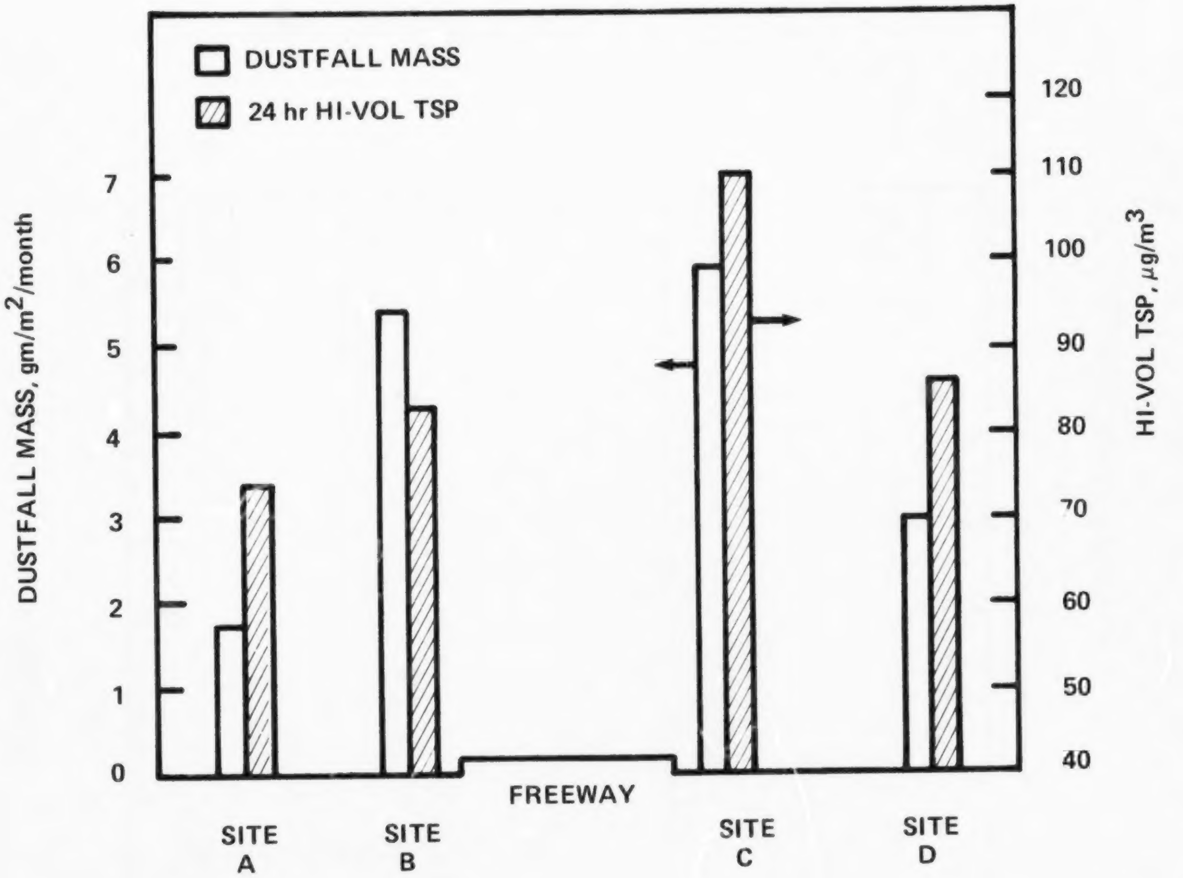


Figure 41. Summer season dustfall - mass.

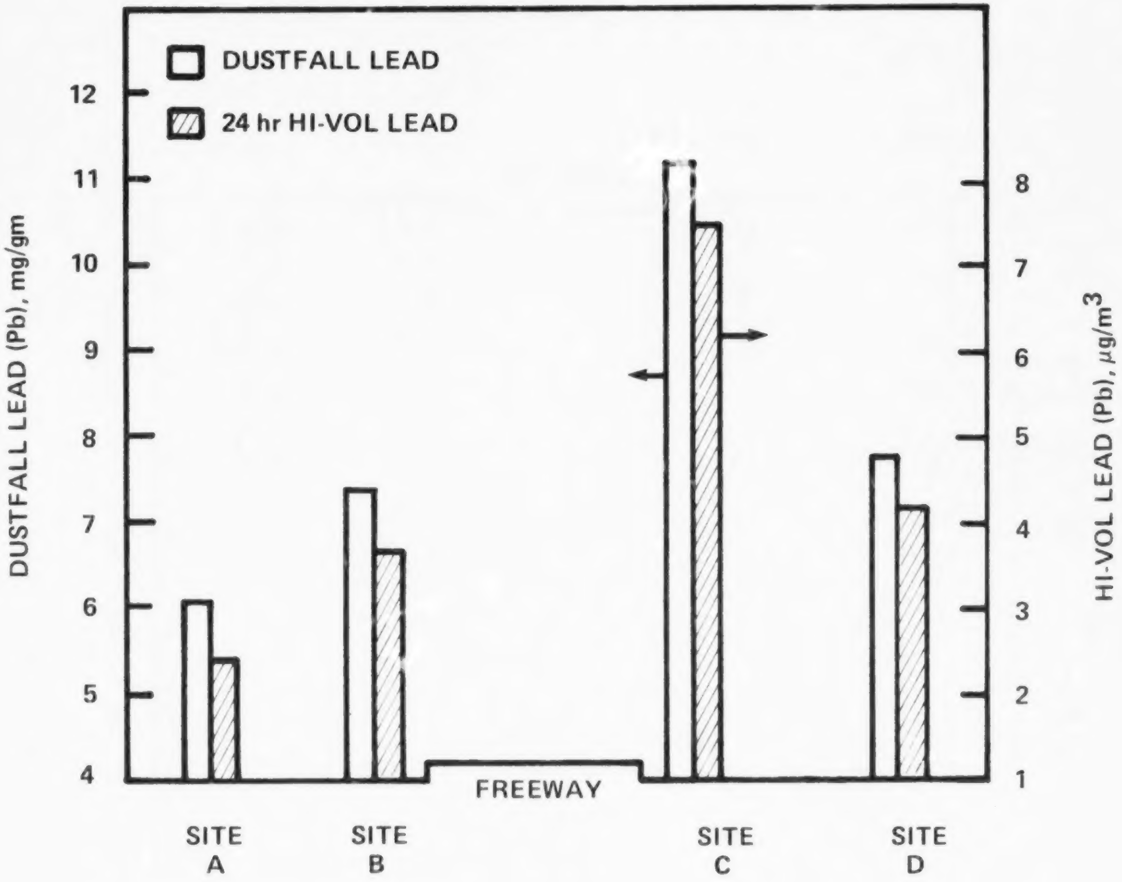


Figure 42. Summer season dustfall - lead.

TABLE IV. PB AND $SO_4^=$ AUTOMOBILE EMISSION TRENDS

	MG/MI			%	
	MASS	PB	$SO_4^=$	PB/MASS	$SO_4^=$/MASS
NON-CATALYST	80	40	<1	50	~0
CATALYST	20(15)	~0	10	~0	50(67)
30% CATALYST	62	28	3	45	5

substantially different than the initial Pb/mass ratio of 50%, and explains why the ratio should have remained essentially constant.

A similar analysis of the $SO_4^=$ contribution from a fleet of 30% catalyst cars shows that an estimated 5% of the mass should be $SO_4^=$. This number is reasonably consistent with the ratios shown in Figure 29 of 2-3%. Because the sulfuric acid/water aerosol emitted from catalyst cars remains as sulfuric acid during analyses for $SO_4^=$ when performing the emission measurements, the equivalent $SO_4^=$ reported is typically one-half of the mass measured. The balance is accounted for by the water in equilibrium. In that the H_2SO_4 aerosol is very reactive and probably has degraded into a sulfate form by the time an ambient sample is analyzed, the numbers in parenthesis in Table IV represent the equivalent masses if the 10 mg/mi of $SO_4^=$ was combined as $(NH_4)_2SO_4$.

The measured decrease in mass emissions from the freeway was unexpected in that this was not a design function of the catalyst. Any beneficial effect from reduction of the total fine particle aerosol emissions must be considered carefully, as the composition of the reduced emission is substantially different (i.e., lead has decreased but sulfate (H_2SO_4) has increased.

ACKNOWLEDGMENTS

The authors wish to acknowledge Franz J. Burmann and Gerald G. Akland for their assistance in reviewing the data and interpreting the results.

STATISTICAL ANALYSIS OF THE LOS ANGELES CATALYST STUDY DATA — RATIONALE AND FINDINGS

George C. Tiao and Steven C. Hillmer

University of Wisconsin
Madison, Wisconsin

ABSTRACT

This discussion presents an analysis of pollutant data gathered in the Los Angeles Catalyst Study. The ultimate purpose is to use the data to determine any increase or decrease in the observed emissions since the introduction of the catalytic converter. An empirical model describes selected observed pollutant concentrations as a function of wind speed, wind direction, traffic counts, and the speed of traffic. Therefore, the analysis takes into account varying traffic patterns and meteorological effects upon the observed pollutant concentrations. The empirical model helps determine any trends in the data after adjusting for changes in the traffic and meteorological conditions.

INTRODUCTION

This paper presents a statistical analysis of the Los Angeles Catalyst Study (LACS) data covering the period June 1974 through November 1976. Our main objective is to assess the effects on the atmospheric concentration of various pollutants due to the introduction of the catalytic converter.

The catalytic converter was adopted by American automobile manufacturers and used on new cars since the 1975 model year. It was designed to reduce the emission of carbon monoxide (CO) and hydrocarbons (HC). Also, new cars equipped with the converter must run on unleaded gasoline. Its use should lead to reduction in lead (Pb) emissions. However, tests have shown (1) that the converter increases the emissions of sulfuric acid which reacts in the atmosphere to form sulfate (SO_4). To study the environmental impact of the catalyst, four air monitoring sites (A,B,C and D), two on each side of the San Diego Freeway (Figure 1), were established by the Environmental Monitoring and Support Laboratory (EMSL) of the Environmental Protection Agency (EPA). Data on a number of pollutants including SO_4, CO and Pb and meteorological variables such as wind speed and wind direction have been collected since June 1974 (2). Also, traffic counts and speeds have been measured since September 1976.

This paper reports our preliminary findings on the following: (1) daily 4 hour afternoon (3-7 p.m.) SO_4 readings (from two different types of sampling equipment (the high-volume (hi-vol) and the membrane samplers); (2) 24 hour hi-vol SO_4 readings; (3) hourly CO readings; and (4) the 4-hour afternoon hi-vol Pb readings. Hourly wind speed and wind direction data for the entire

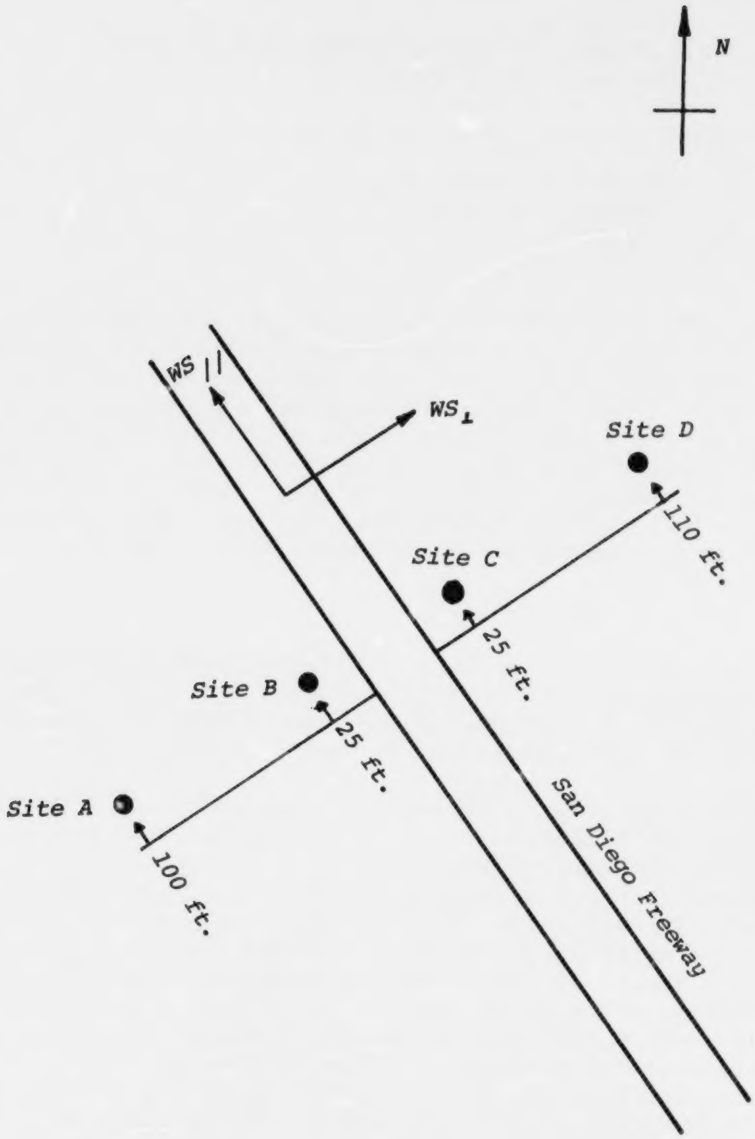

N
WS ||
WS ⊥
Site D
110 ft.
Site C
25 ft.
Site B
25 ft.
Site A
100 ft.
San Diego Freeway

Figure 1. Simplified map of the air monitoring sites.

period, and the available hourly traffic counts and traffic speed for the period September 1976 through November 1976 will be used in our analysis.

In the discussion of analysis of SO_4 data, a preliminary examination of 4 hour hi-vol, 4 hour membrane and 24 hour hi-vol SO_4 data is presented. The next discussion concerns CO data and, in particular, presents an empirical-mechanistic model relating the CO readings at site C to wind speed, wind direction, and traffic counts and speeds. The model is used to assess the trend in CO emissions since June 1974. Next, the 4 hour hi-vol Pb data are analyzed. In particular, the model developed for CO is extended to the Pb data for assessing the trend.

PRINCIPAL FINDINGS

Our principal findings are as follows:

1. $\underline{SO_4}$

   (i) *The background level (from sources other than the freeway) of SO_4 decreased from 1974 to 1976.*

   (ii) *The across the freeway difference of the 4 hour hi-volume readings decreased from 1975 to 1976.*

   (iii) *The across the freeway differences for both the 4 hour membrane and the 24 hour hi-volume readings increased from 1975 to 1976.*

   (iv) *The 4 hour hi-volume data appear to be measuring something different than the 4 hour membrane data. Further research seems necessary to determine the cause of this discrepancy.*

2. *CO*

   (i) *There appears to have been a decrease in CO emissions from 1975 to 1976.*

3. *Pb*

   (i) *There was a steady decrease in Pb emissions from 1974 to 1976.*

   (ii) *At site C the average 3-7 p.m. concentration level is about 60% higher on the weekends than that for the weekdays.*

ANALYSIS OF SO_4 DATA

Data on SO_4 consist mainly of daily 4 hour afternoon (3-7 p.m.) readings from the hi-vol sampler and the membrane sampler, and the daily 24 hour hi-vol readings. The 4 hour readings are of particular interest since, during the afternoon hours, the wind is usually blowing in a direction roughly perpendicular to the freeway (2,5) with the result that the difference in readings between sites across the freeway should reflect contributions from the freeway traffic.

As an initial step in the analysis of the SO_4 data, we have employed daily readings to calculate monthly averages at various sites. In computing monthly averages, extreme observations were eliminated according to the following procedure. For a particular month, let Y be an observation, $\bar{Y}$ be the average and s the estimated standard deviation of Y. If $|Y_i-\bar{Y}|>3s$, Y_i will be excluded and then $\bar{Y}$ and s recalculated. The process will be repeated until all observations fall with $\bar{Y} \pm 3s$.

ANALYSIS OF MONTHLY MEANS

The monthly averages of the 4 hour hi-vol readings at sites A to D are shown by the solid lines in Figure 2(i) to (iv), respectively. From these plots we make the following observations.

(1) At each location there appears to have been a decrease in the SO_4 readings from 1974 to 1976.

(2) The monthly means at the sites C and D downwind from the freeway, are higher than those for the upwind sites A and B, indicating a contribution of SO_4 from the freeway traffic.

(3) The freeway contribution is, however, very small when compared to the average level of SO_4 across these four sites.

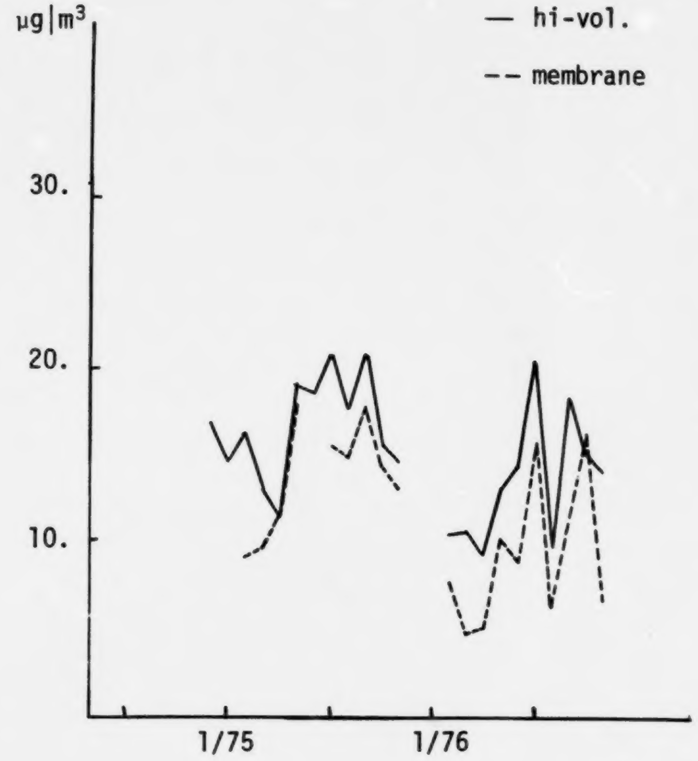
Next, the monthly means of the 4 hour membrane data for sites A and C are given by the dotted lines in Figures 2(i) and (iii). Similar to the 4 hour hi-vol data, at both sites the level decreased from 1975 to 1976. Finally, the monthly means of the 24 hour hi-vol readings at sites A and C are shown in Figures 2(v) and (vi). Again the level of SO_4 at both sites decreased during the data period.

COMPARISON OF THE HI-VOLUME AND MEMBRANE READINGS

It is of interest to compare the 4 hour hi-vol and membrane readings. Figures 2(i) and (iii) show that while the seasonal patterns of these two readings are similar, the hi-vol means are consistently higher than the membrane means. For further comparison, Figures 3(i) and 3(ii) show, respectively for sites A and C, the scatter plots of the daily 4 hour membrane vs. hi-vol readings. We observe that for site A the points fall close to a line with a slope approximately equal to 1 and an intercept of about $4\mu g/m^3$. On the other hand, for site C the points are again close to a line but having a slope of about 0.8 and an intercept of 7.7 $\mu g/m^3$. These figures strongly suggest that the membrane and the hi-vol readings are systematically biased and that the nature of the bias is different at different sites.

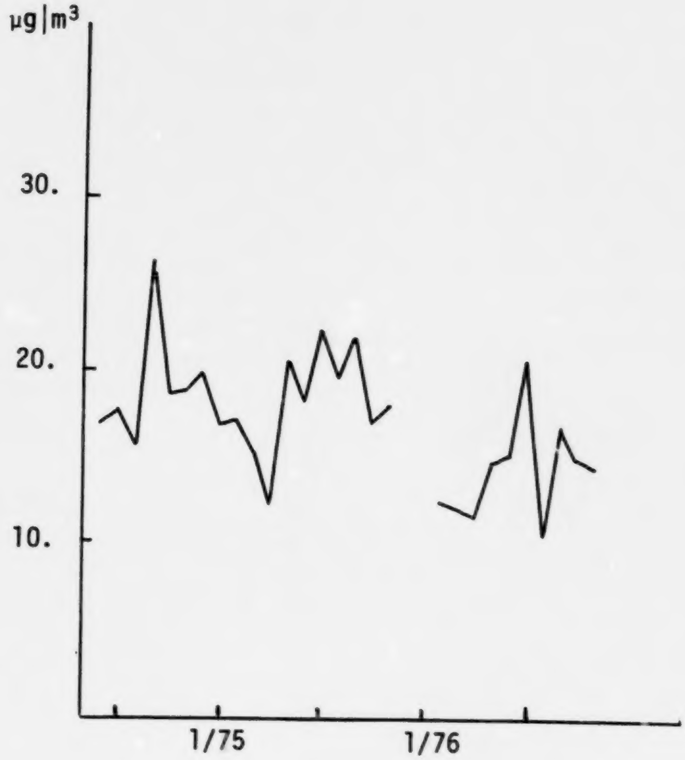
ACROSS THE FREEWAY DIFFERENCES

We next consider the monthly means of the across the freeway difference (C-A) of SO_4 for the 4 hour hi-vol, the 4 hour membrane and the 24 hour hi-vol readings. These means are plotted in Figures 3(iii)-(v). We observe that: (1) The 4 hour hi-vol readings indicate a decrease in the across the freeway



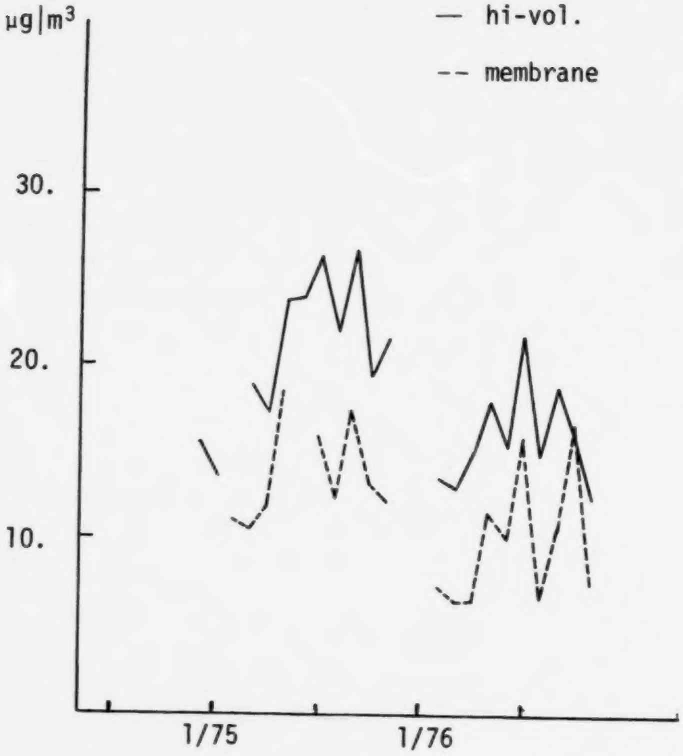
(i) Site A.

Figure 2. Monthly means of 4-hr hi-vol. and membrane afternoon readings of SO_4 for various sites.



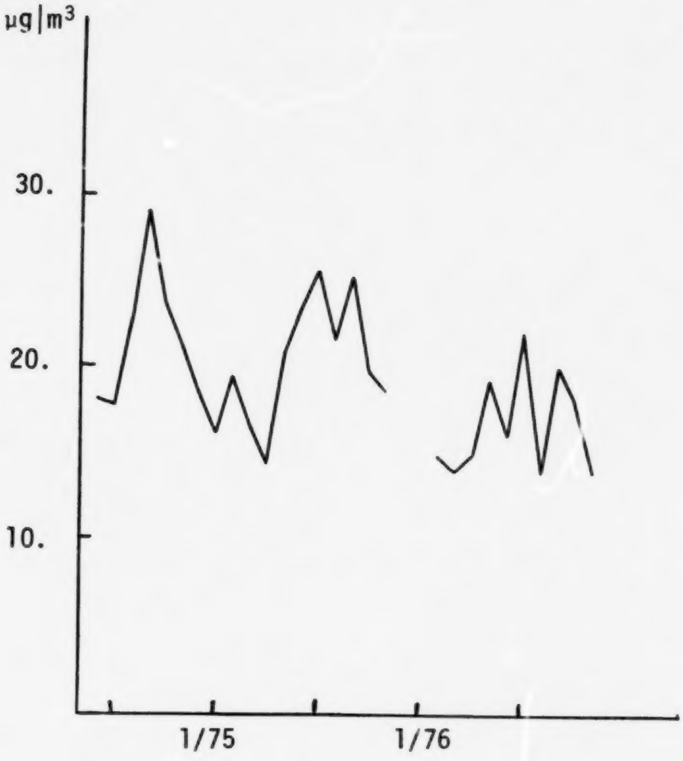
(ii) Site B.

Figure 2. Monthly means of 4-hr hi-vol. and membrane afternoon readings of SO_4 for various sites.



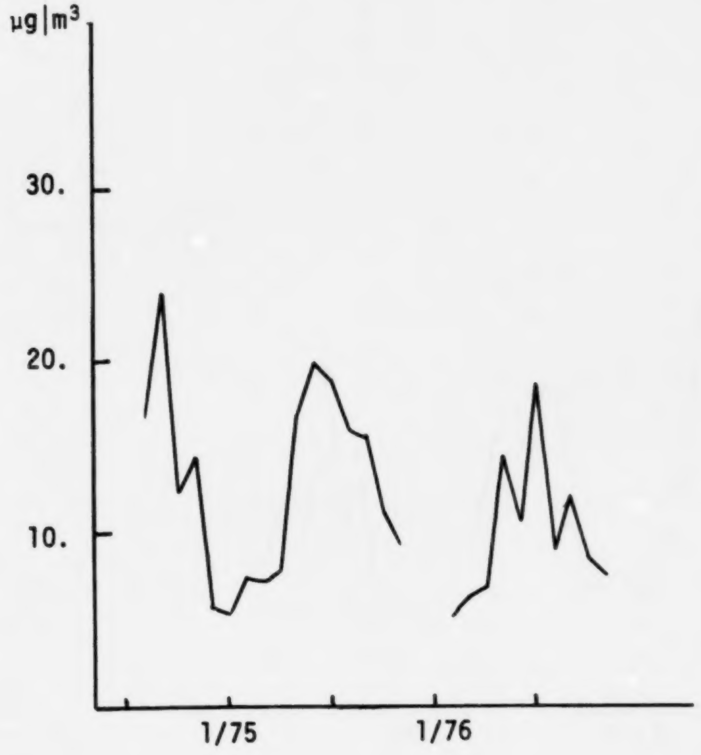
(iii) Site C.

Figure 2. Monthly means of 4-hr hi-vol. and membrane afternoon readings of SO_4 for various sites.



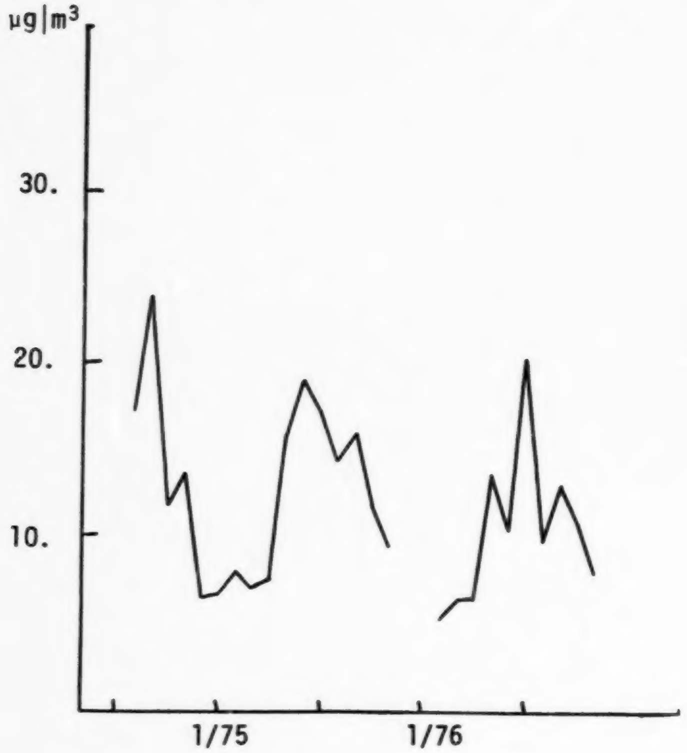
(iv) Site D.

Figure 2. Monthly means of 4-hr hi-vol. and membrane afternoon readings of SO_4 for various sites.



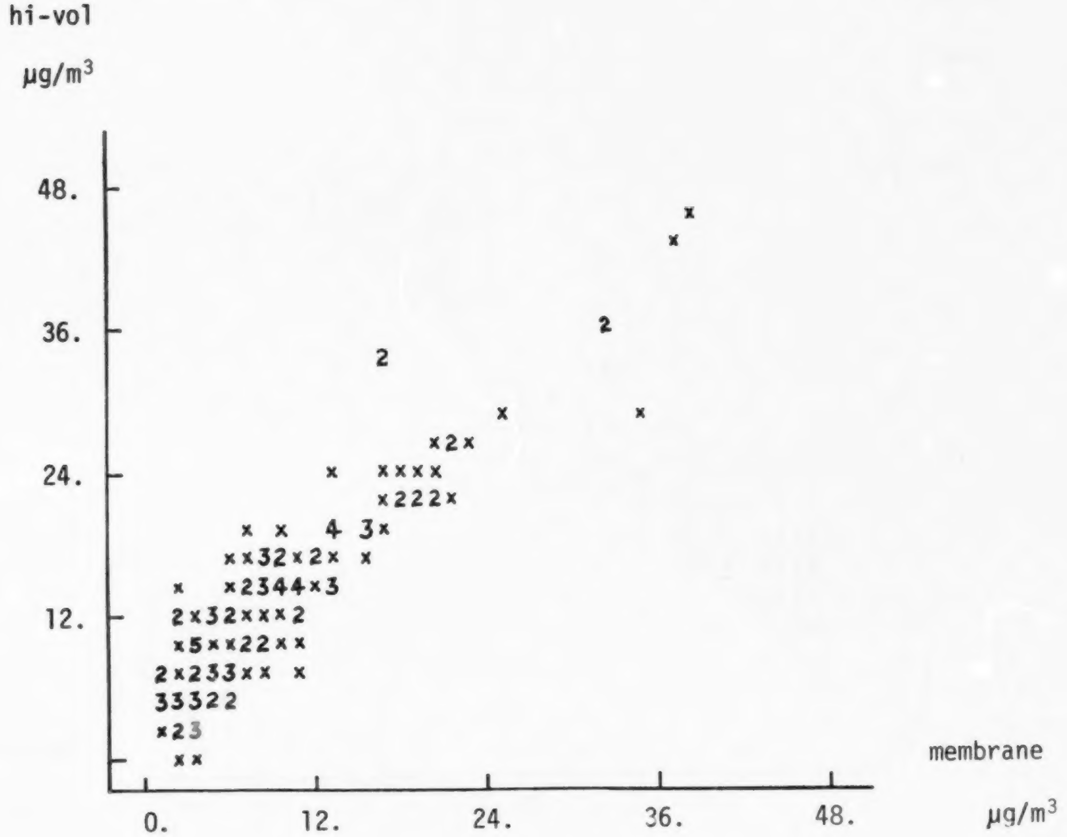
(v) Site A.

Figure 2. Monthly means of 24-hr hi-vol readings of SO_4.



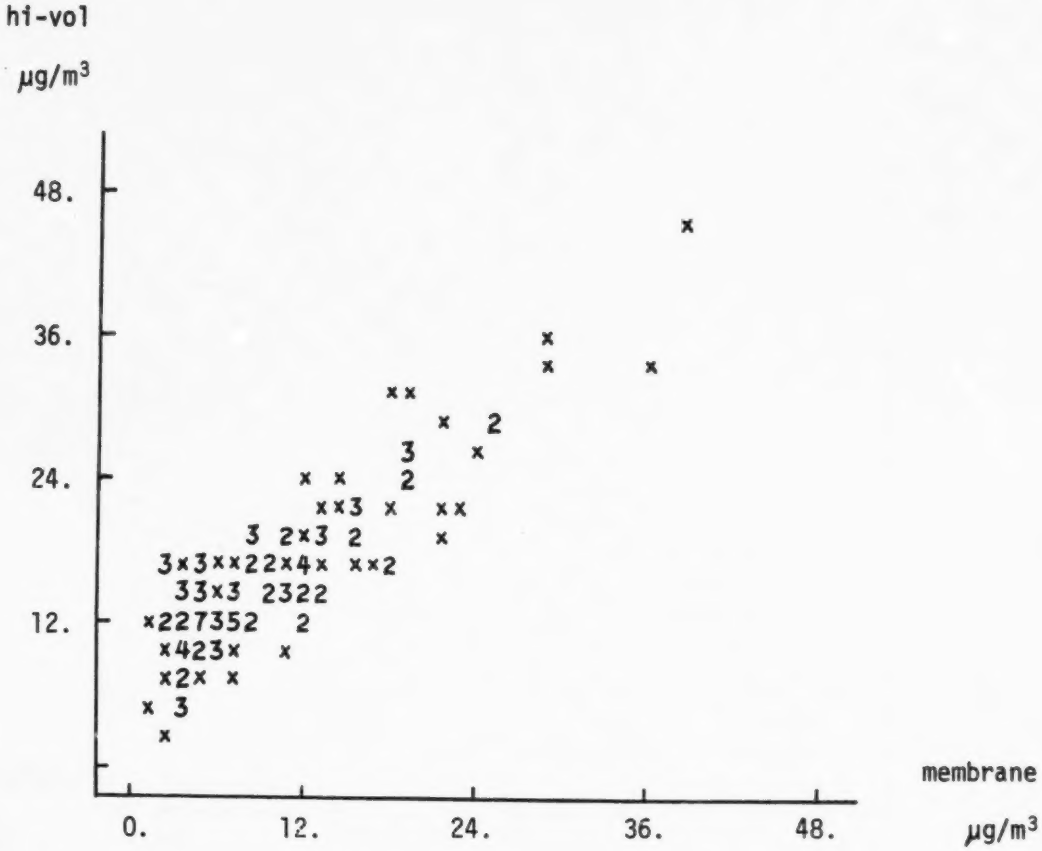
(vi) Site C.

Figure 2. Monthly means of 24-hr hi-vol. readings of SO_4.



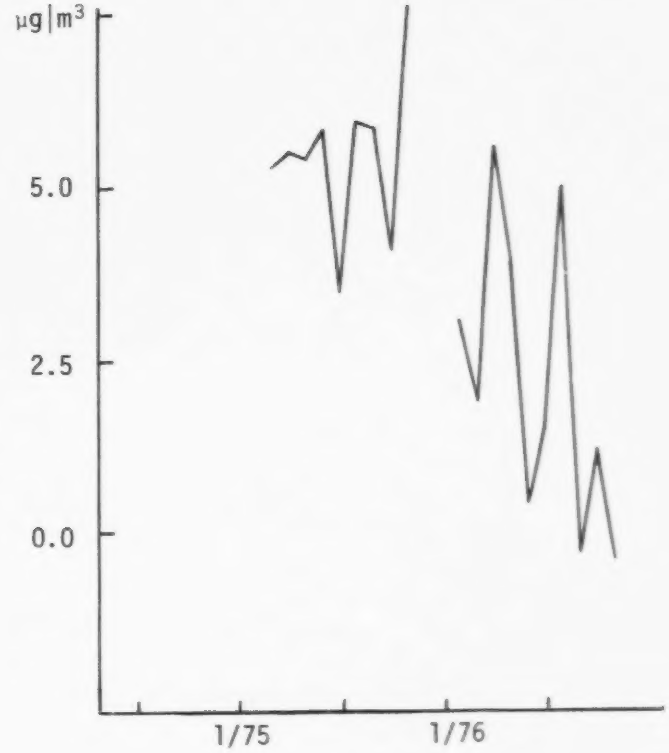
(i) Site A.

Figure 3. Scatter plots of hi-vol. vs. membrane SO_4.



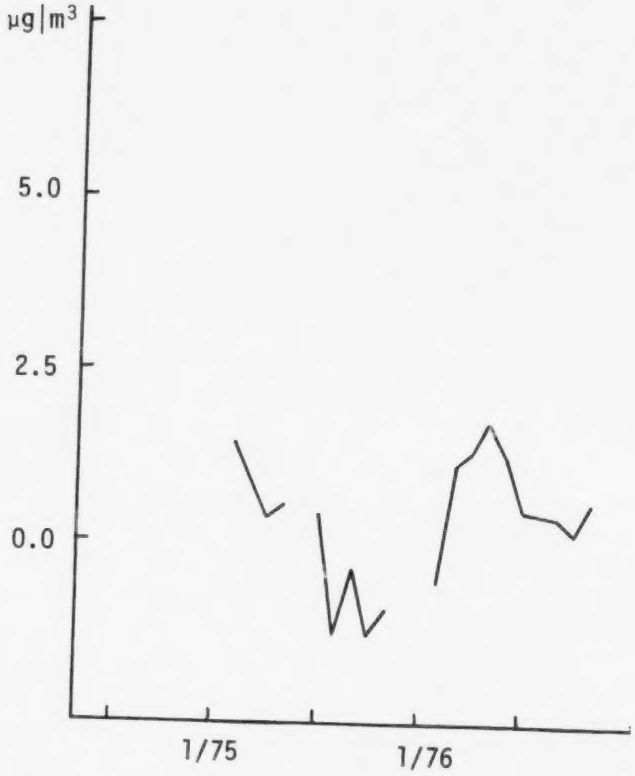
(ii) Site C.

Figure 3. Scatter plots of hi-vol. vs. membrane SO_4.



(iii)

Figure 3. Monthly means of 4-hr hi-vol. SO_4 (C-A).



(iv)

Figure 3. Monthly means of 4-hr membrane SO_4 (C-A).

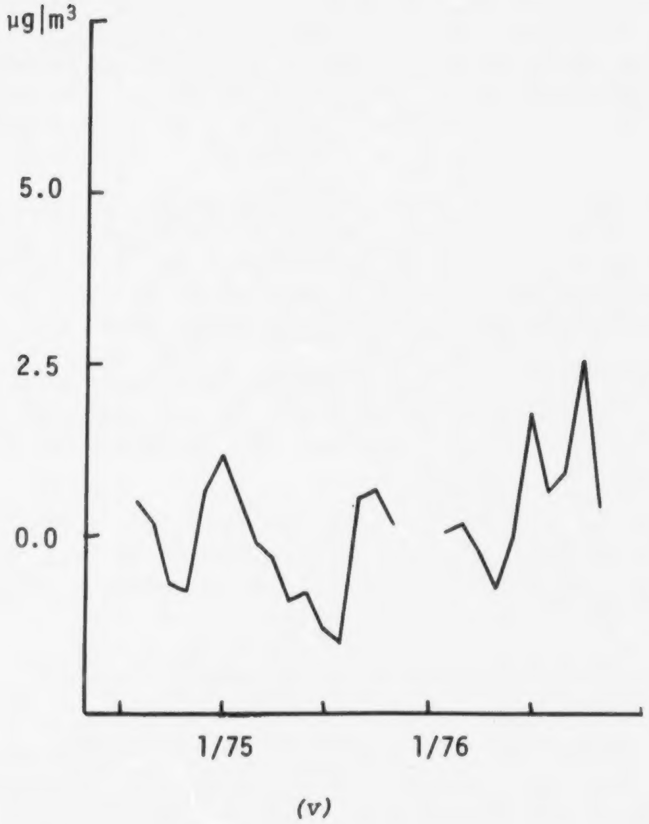


Figure 3. Monthly means of 24-hr hi-vol. SO_4 *(C-A).*

differences from 1975 to 1976. (2) On the other hand, the 4 hour membrane readings indicate that there was an increase in the across the freeway difference from 1975 to 1976. (3) The 24 hour hi-vol readings also show an increase from 1975 to 1976. These observations are partially confirmed by the t-values given in Table I for comparing the overall means of the across the freeway differences (C-A) for the months June through October between 1975 and 1976. Specifically, the t-values indicate that the increase in the 4 hour hi-volume readings and the decreases in the other two measurements are real.

The sample means and standard deviations given in the table also show that for each year, the across the freeway differences in the 4 hour hi-vol readings are considerably larger than those for the other two. Thus, both in terms of the level and the trend, the 4 hour membrane measurements and the 24 hour hi-vol measurements are in close agreement, but they are incompatible with the 4 hour hi-volume readings.

A Conjecture

The preceding analysis raises a number of perplexing questions. First, how can we account for the discrepancies between the different methods of measuring SO_4? Second, which, if any, of the methods are giving correct pollutant readings? These questions must be answered before any conclusions about trends in the across the freeway difference can be made.

According to one researcher (6), SO_2 can react on filters used in the hi-vol sampler to form SO_4, and this may be a reason for the observed discrepancies. One possible theory that could explain what we have observed runs as follows:

- The 4 hour hi-volume difference (C-A) is mostly SO_4 formed by SO_2 reacting on the filter. This artifact formation progresses more quickly at site C in the afternoon because of exposure to additional SO_2 from the freeway.

- The artifact formation occurs to a lesser extent, if at all, on the membrane filter.

- After a sufficiently long time the artifact formation of SO_4 will be about equal at sites A and C so that the 24 hour hi-volume difference represents largely contributions from the freeway.

Although this theory could explain to a certain extent the observed discrepancies, further research seems necessary to determine the precise nature of these two sampling methods.

Conclusions

We can tentatively conclude from our analysis that (1) there is a substantial difference between the 4 hour hi-vol and membrane SO_4 readings, and (2) from the available data there is a small amount of SO_4 being contributed from the freeway traffic.

Table I. COMPARING THE MEANS OF THE ACROSS THE FREEWAY DIFFERENCES BETWEEN 1975 AND 1976

	June-Oct. 1975			June-Oct. 1976			Difference 1975-1976	
	mean	s.d.	no.of obs.	mean	s.d.	no.of obs.	t-value	sig-level
4 hour hi-volume	5.11	4.45	143	2.22	3.74	133	5.86	.0000
4 hour membrane	- .40	1.82	36	1.00	1.56	119	-4.15	.0001
24 hour hi-volume	-1.32	1.54	123	.45	1.80	125	-8.28	.0000

ANALYSIS OF THE CO DATA

CO data consist of hourly readings at sites A and C. As a preliminary step in our analysis, monthly means of the daily 4 hour (3-7 p.m.) averages were determined and they are shown in Figures 4(i) and (ii) for sites A and C, respectively. From these figures we can make the following observations: (1) The behavior of CO is markedly seasonal, being higher in the winter months than in the summer months. Thus, any trend analysis must make proper allowance for the seasonal effect. (2) The level at site C is considerably higher than that at site A. (3) At site A the level is particularly low in the summer months, about .5 ppm. Since we are mainly interested in the freeway contribution of CO, in what follows we will concentrate our analysis on the downwind site, C.

Two major factors influencing the behavior of CO are traffic and the wind (3,5,7). These two factors must be taken into account in studying the effect of the catalytic converter. We have available hourly readings of (i) wind speed and wind direction for the entire period, and (ii) traffic counts and traffic speeds for the period September through November 1976. In what follows we built an empirical-mechanistic model (8) to describe the observed CO concentrations at site C as a function of the wind and traffic. The model will then be used to assess the trends in CO emissions.

MOTIVATION FOR THE MODEL

Figure 4(iii) gives the average diurnal curves of CO at site C computed from the following three data periods:

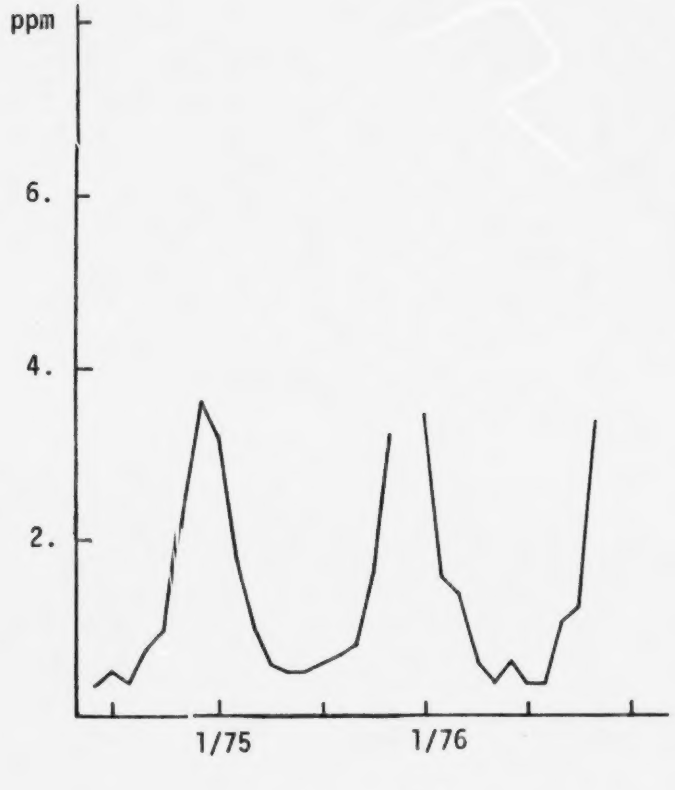
(i) summer weekday: Mondays-Thursdays, June-October 1975

(ii) summer weekend: Sundays, June-October 1975

(iii) winter weekday: Mondays-Thursdays, December 1974-April 1975.

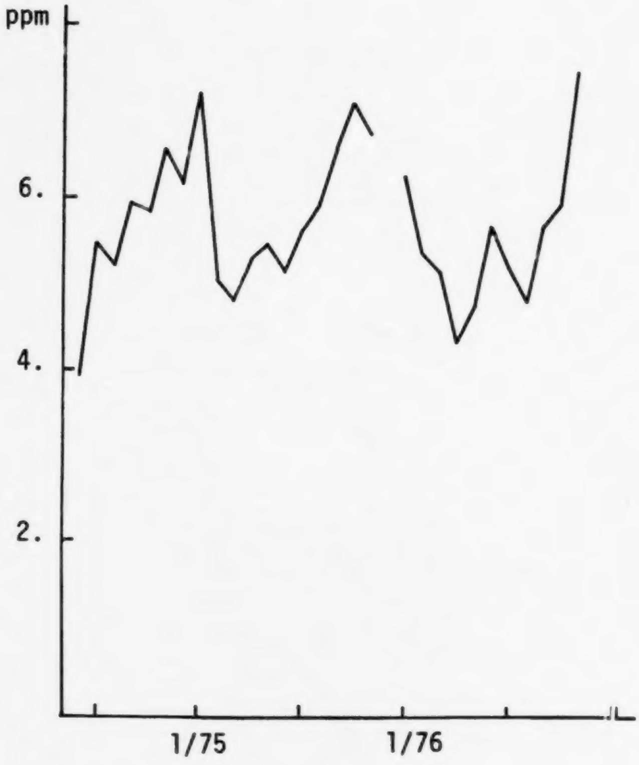
These three diurnal curves illustrate that the behavior of CO changes from weekday to weekend and from summer to winter. The summer weekday curve has two peaks which roughly correspond to the morning and afternoon rush hours. In contrast, the summer weekend plot fails to have these peaks. The diurnal behavior of CO also changes from summer weekday to winter weekday, the most notable change being the absence of a peak corresponding to the morning rush hours in the winter.

In Figure 4(iv) the dotted line gives the diurnal pattern of the average counts of vehicles passing the monitoring sites on weekdays. The figures shown are average counts for each hour of weekdays (Monday-Thursday) obtained during the period September 1976 through November 1976. Since this is the only period for which traffic data are available and the traffic patterns in Los Angeles are not expected to vary much over time, we will for the moment assume that the figures shown are applicable to the entire period (June 1974-November 1976) under study.



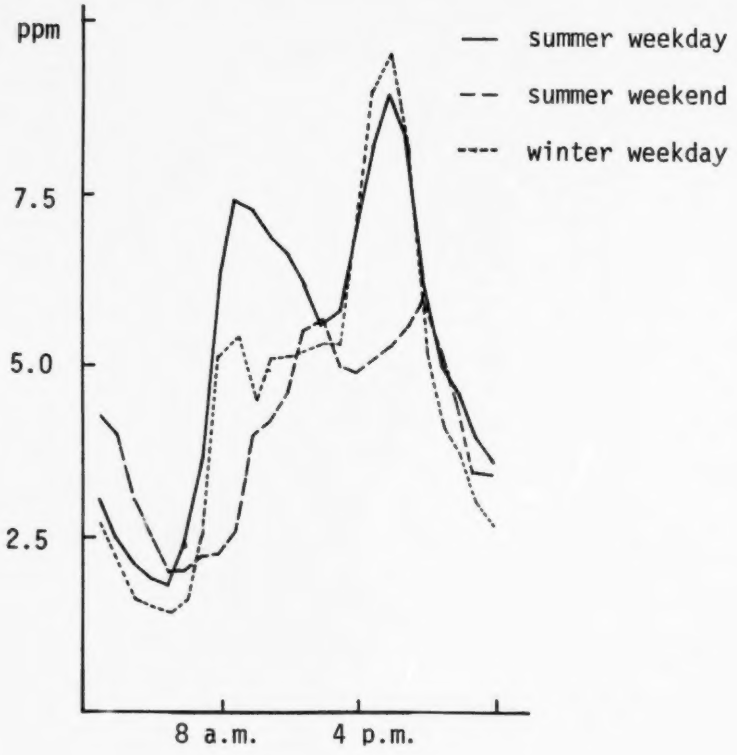
(i) Site A.

Figure 4. Monthly means of 4-hr (3 p.m. - 7 p.m.) CO.



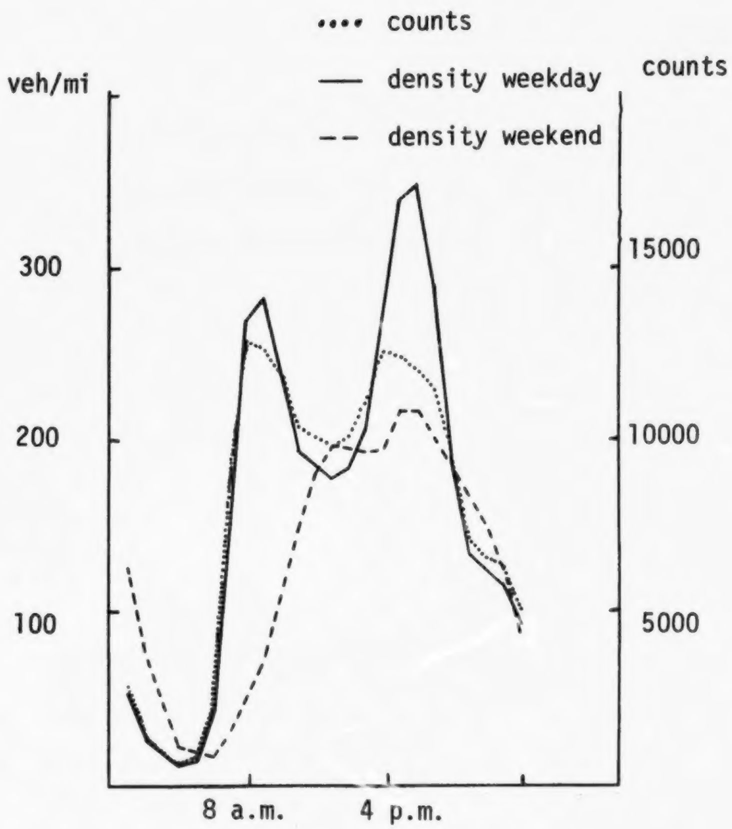
(ii) Site C.

Figure 4. Monthly means of 4-hr (3 p.m. -- 7 p.m.) CO.



(iii)

Figure 4. Diurnal plot of CO, Site C.



(iv)

Figure 4. Diurnal plot of traffic.

Comparing the diurnal pattern of the weekday counts with that of the summer weekday CO, we observe that the counts do not seem to reflect the magnitude of CO during the evening rush hours. A possible reason for this is the increase in traffic congestion during that time. The solid curve in Figure 4(v) shows the diurnal pattern of the traffic speed for weekdays. Notice the two dips during the morning and the evening rush hours and the difference in magnitude between them. Thus, there is a large volume of traffic moving very slowly during the evening rush hours, and the vehicle counts do not accurately reflect the density of the traffic.

TRAFFIC DENSITY

To more appropriately reflect the situation, we consider the traffic density (TD) defined as

$$TD = \frac{\text{number of vehicles passing the sites per hour}}{\text{average speed per hour}}$$

which is a measure of the intensity of traffic around the sites (in units of vehicles per mile). The solid line in Figure 4(iv) shows that the diurnal pattern of TD for weekdays seems to match the CO pattern much better than the vehicle counts. In addition, for the weekends, the diurnal pattern of TD shown by the dashed line in Figure 4(iv) also correlates with that of CO given in Figure 4(iii). From the above discussion it appears that the observed concentrations of CO are approximately proportional to TD.

THE WIND VECTOR

Another major factor influencing the pollutant readings is the speed and direction of the wind. Data on wind speed and wind direction are available on an hourly basis. Following (5) we have decomposed the observed hourly wind vector at site A into two components: one which is perpendicular to the freeway ($WS_\perp$) and the other parallel to it ($WS_\parallel$). The positive directions for the two components are shown in Figure 1. Specifically, let WS be the wind speed and WD the wind direction. (WD = 0 when the direction is due north). Then, since the freeway is situated at approximately 235° from the north, we have that

$$WS_\perp = WS \cdot \cos(WD - 235^\circ)$$

$$WS_\parallel = WS \cdot \sin(WD - 235^\circ).$$

The diurnal patterns of $WS_\perp$ for the summer months (June-October 1975) and the winter months (December 1974-April 1975) are plotted in Figure 4(vi). We observe that the $WS_\perp$ in the winter is lower than that in the summer. In particular, for the winter, from midnight to 9 a.m. the $WS_\perp$ is negative so that the wind is blowing away from site C. The $WS_\perp$ for the same hours in the summer months is nearly zero. This change in the $WS_\perp$ from the summer to the winter could explain the absence of a peak in CO during the morning rush hours in the winter (see Figure 4(iii)). Therefore, it appears that seasonal changes in $WS_\perp$ may account for the observed changes in the diurnal behavior of CO from the summer to the winter.

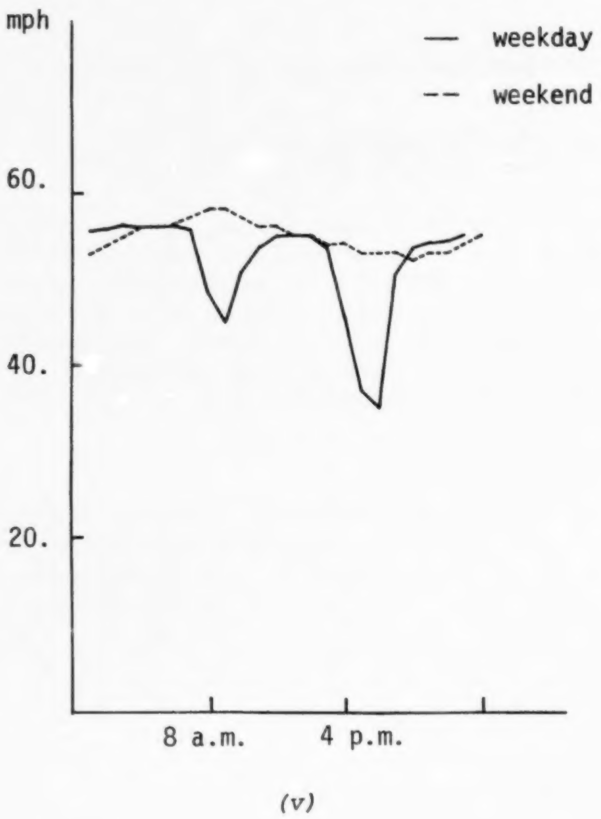
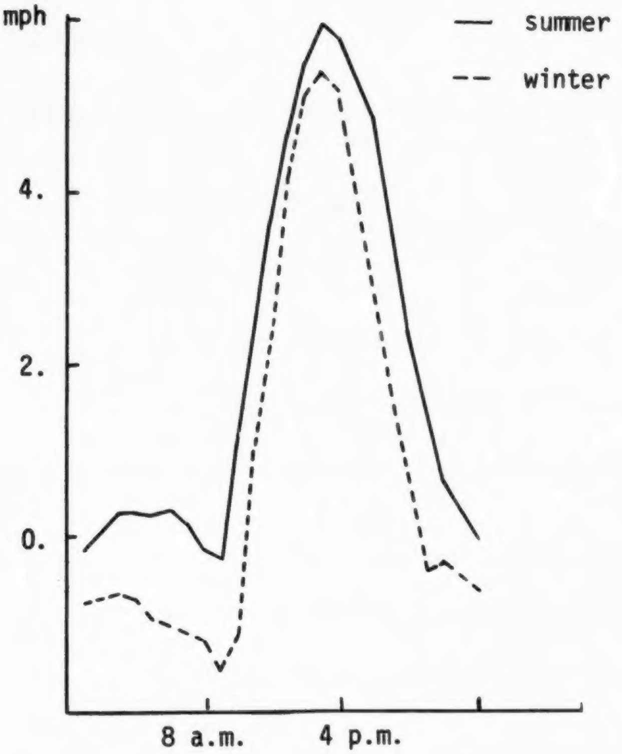


Figure 4. Diurnal plot of traffic speed.



(vi)

Figure 4. Diurnal plot of $WS_{\perp}$.

In order to determine more precisely the effect of $WS_{\perp}$ on CO, we have divided all the available hourly $WS_{\perp}$ readings into intervals of .5 mile per hour. For each interval we have calculated the average of the corresponding CO readings. These averages are plotted in Figure 5(i). Observe that a convenient way to characterize the dependency of CO on WS is to take CO proportional to the dispersion factor

$$e^{-b(WS_{\perp}-W_o)^2},$$

where b and W_o are two appropriate constants.

THE CO MODEL

The above considerations have led us to consider the following tentative model for the diurnal behavior of CO at site C:

$$CO_t = \alpha + K\cdot(TD_t)\cdot e^{-b(WS_{\perp t}-W_o)^2} + a_t$$

where

CO_t: the observed CO for site C at hour t.

TD_t: the traffic density at hour t.

$WS_{\perp t}$: the perpendicular component of the wind vector at hour t.

a_t: an added error term for hour t.

α: a parameter measuring the background CO.

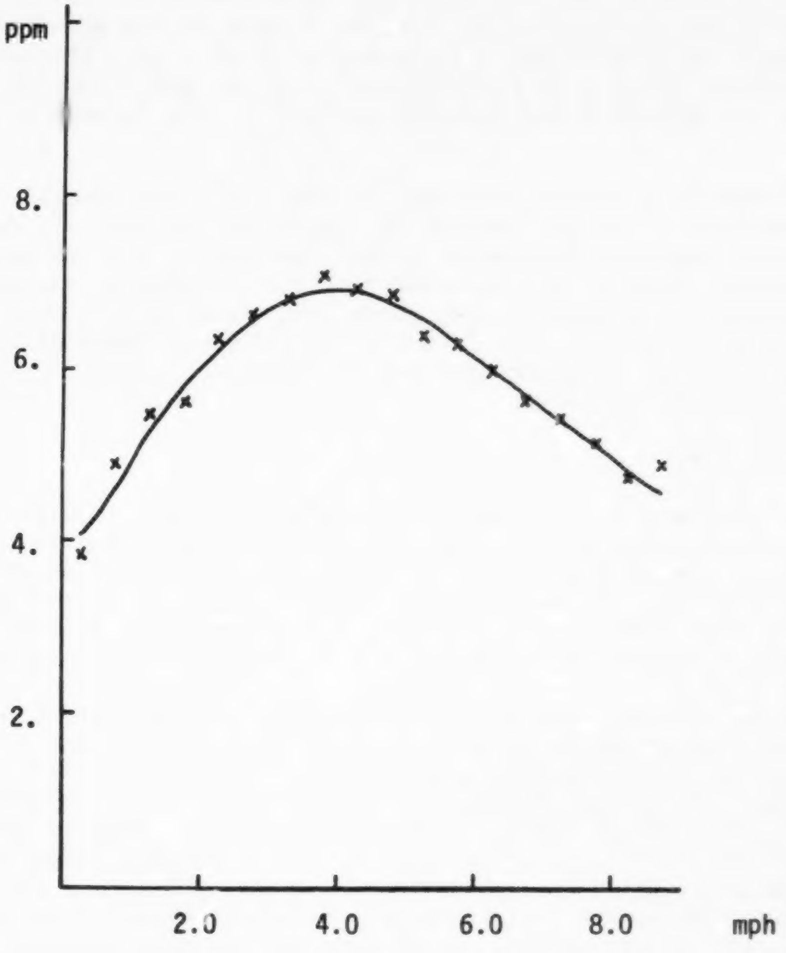
K: a parameter proportional to emissions.

$e^{-b(WS_{\perp t}-W_o)^2}$: a diffusion factor involving the perpendicular wind component and two parameters b and W_o.

Given a set of data on CO, $WS_{\perp}$ and TD, the parameters can be estimated by employing standard non-linear procedures. Specifically, on the assumption that the errors a_t's are independently and normally distributed with mean zero and variance σ^2, (α, K, b, and W_o) are estimated by minimizing the sum of squares of the a_t's with respect to these parameters simultaneously.

Testing the Model

The model is useful for our purposes due to the following: (1) It is a relatively simple model with only four parameters to be estimated from the data. (2) It takes into account the effects of the traffic and the wind. (3)



(i)

Figure 5. Plot of CO vs. $WS_{\perp}$

The parameter K has an important interpretation. It is proportional to emissions, and hence it will play a crucial role in determining if there has been significant changes in emissions over time.

However, before we use the model for trend assessment, it is important to verify that it can in fact account for the changes in the observed behavior of CO from weekday to weekend and from summer to winter. For this purpose, we have employed the three sets of CO average readings shown earlier in Figure 4(iii), the corresponding $WS_{\perp}$ averages and the TD values given in Figure 4(iv).

The parameter estimates are shown in Table II. The actual CO readings and the predicted values are plotted in Figures 5(ii)-(iv). It seems that the model produces very close agreement between the actual and the predicted in all three cases. Notice from Table II that for the weekend the estimated emission constant K is considerably lower than those for the weekdays. This is perhaps due to the fact that CO emissions may also depend on the driving model (in particular, accelerations and decelerations) which is very different between weekdays and weekends.

Evaluation of Trend

Our main objective is to assess the effect of the catalytic converter on ambient CO concentrations. This can be done in terms of the model ideally by allowing the parameter K to depend on the fraction of vehicles equipped with catalytic converters. Since precise estimates of the fractions of catalyst cars are not available, we shall proceed with a trend analysis by investigating possible changes in the value of K over different time periods.

As a first attempt, the model has been used for evaluation of trends as follows. We divided the entire time span of the data into the following five periods: (1) June 1974 through October 1974, (2) November 1974 through April 1975, (3) May 1975 through October 1975, (4) November 1975 through April 1976 and (5) May 1976 through October 1976. This division roughly corresponds to the "summer" and the "winter", and each period is of sufficient length to allow for an appreciable increase of catalyst equipped cars. The emission parameter K was allowed to vary from period to period but the other parameters, α, b *and* W_o*, were constrained to be the same for all five periods. The weekday data were employed in estimating the parameters. Within each period we calculated the 24 hourly averages of CO and* $WS_{\perp}$ *for each of the three consecutive two month segments. (For the first period, we took averages for June, then July and August, finally September and October.) The CO and* $WS_{\perp}$ *averages for all five periods together with the averages of the available weekday TD were then employed to estimate the parameters* $\alpha, b, W_o, K_1, \ldots, K_5$ *where* K_j *is the emissions parameter in period* j *for* $j = 1, \ldots, 5$*. In addition, we used a weighted least squares estimation procedure to allow for possible changes in the variance from period to period. The parameter estimates are given in Table III.*

Consider the changes in the emission parameter K over these 5 periods. We see from Table III that the estimated K decreased between the first and the

Table II. CO MODEL TEST FITS

June 1975-October 1975 Weekdays (M-R)

Parameter	Estimate	Std. Err.
α	1.90	.14
b	.00035	.00005
W_O	3.27	.13
K	.0241	.00096

June 1975-October 1975 Sunday

Parameter	Estimate	Std. Err.
α	1.79	.23
b	.00013	.00011
W_O	2.54	1.11
K	.0190	.0016

December 1974-April 1975 Weekdays

Parameter	Estimate	Std. Err.
α	1.42	.17
b	.00029	.00006
W_O	2.89	.26
K	.0228	.0010

Table III. ASSESSMENT OF CO TREND

Period	Parameters	Estimate	Std. Err.
	α (ppm)	1.71	.076
	b	.00026	.00002
	W_o (mph)	2.93	.098
Summer 74	K_1 ($\mu g/m^2$)	.0195	.0006
Winter 74-75	K_2 ($\mu g/m^2$)	.0235	.0008
Summer 75	K_3 ($\mu g/m^2$)	.0245	.0007
Winter 75-76	K_4 ($\mu g/m^2$)	.0196	.0008
Summer 76	K_5 ($\mu g/m^2$)	.0209	.0006
	σ_1	.68	
	σ_2	.88	
	σ_3	.66	
	σ_4	.90	
	σ_5	.63	

second winters, and also between the second (1975) and the third (1976) summers. This can be associated with the increase in the number of catalyst cars. On the other hand, the increase in K between the first and the second summers, from .0195 to .0245, is somewhat surprising. This anomaly may very well be due to the fact that the same TD data were used for all five periods. While the traffic pattern is not expected to vary much over time in Los Angeles, because of the energy crisis, the (estimated) total traffic volume did show a slight dip in 1974, from 182,500 in 1973 to 180,000 in 1974 and to 182,500 in 1975*. Thus, there was an increase of about 1% from 1974 to 1975. In the meantime, a major change in the speed limit occurred around January, 1975, from 70mph to 55mph, representing roughly a 20% decrease. Since TD is the ratio of traffic counts over average speed, the density figures used in the estimation contain a considerable upward bias for the first period and could account for most, if not all, of the increase in K from 1974 to 1975.

Conclusions

We have developed a model which relates the observed behavior of CO at site C to traffic density and the perpendicular wind component. By using this model to assess the trend in CO, we conclude that CO emissions decreased from 1975 to 1976 by about 15%.

ANALYSIS OF THE Pb DATA

This section presents a preliminary analysis of the lead readings. The Pb data consist mainly of the 4 hour afternoon hi-volume readings from June 1974-October 1976. Hi-volume readings for 4 morning hours were also collected during the period June 1974-January 1976**. To begin with, we consider the monthly means of the weekdays (Monday through Thursday) afternoon readings. These monthly averages for sites A through D are plotted in Figures 6(i) through (iv), respectively. It is clear that the levels at sites C and D are much higher than those at A and B. Also, in the summer months there is very little Pb at these latter sites. As in the case of CO we shall concentrate our analysis on the downwind sites, C and D.

For both site C and site D the level of Pb in the summer months appears to have steadily decreased from 1974 to 1976. Table IV shows that these decreases are statistically significant.

EXTENSION OF MODEL TO Pb DATA

The model developed for hourly CO data can be readily extended to the 4 hour Pb readings. This is achieved by summing the right hand side over the 4 afternoon hours to obtain

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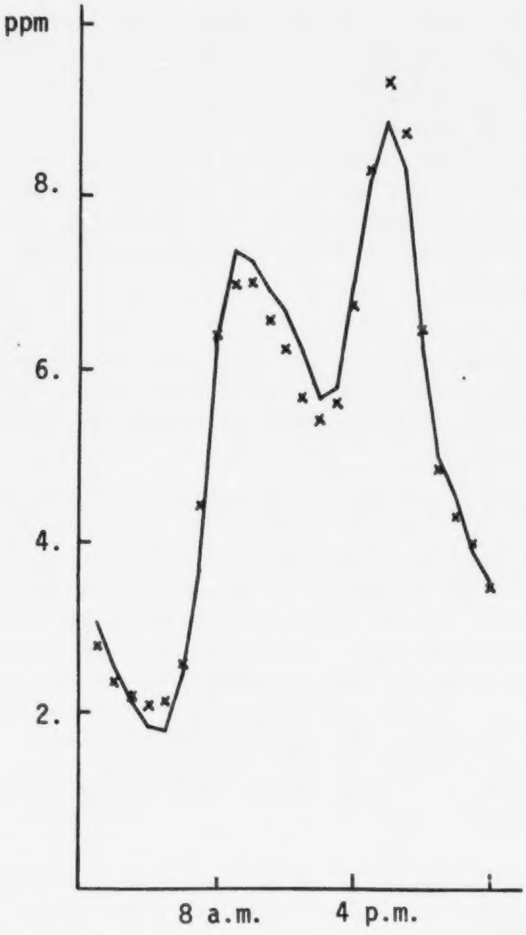
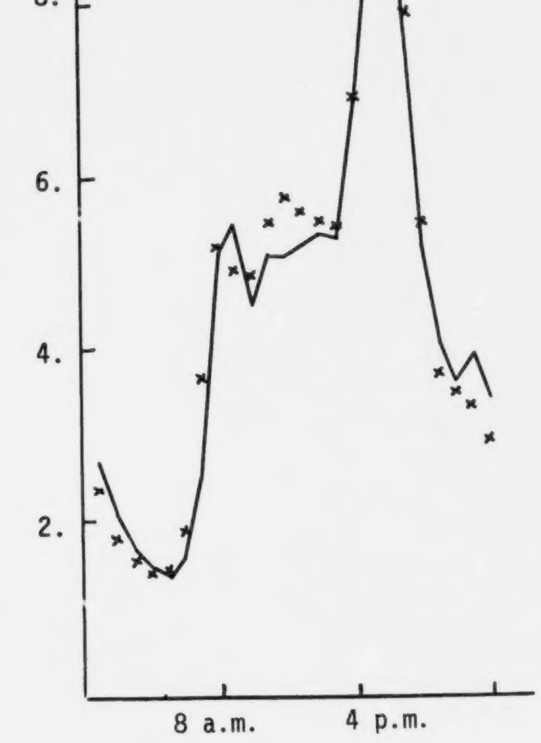
*These are estimated daily traffic totals near the sampling sites obtained from the State of California Department of Transportation publications "Traffic Volume on California State Highways" for 1973, 1974 and 1975.

**Samplers operated 6-10 a.m. from June 1974 to January 1975 and 8-12 a.m. from January 1975 through January 1976.



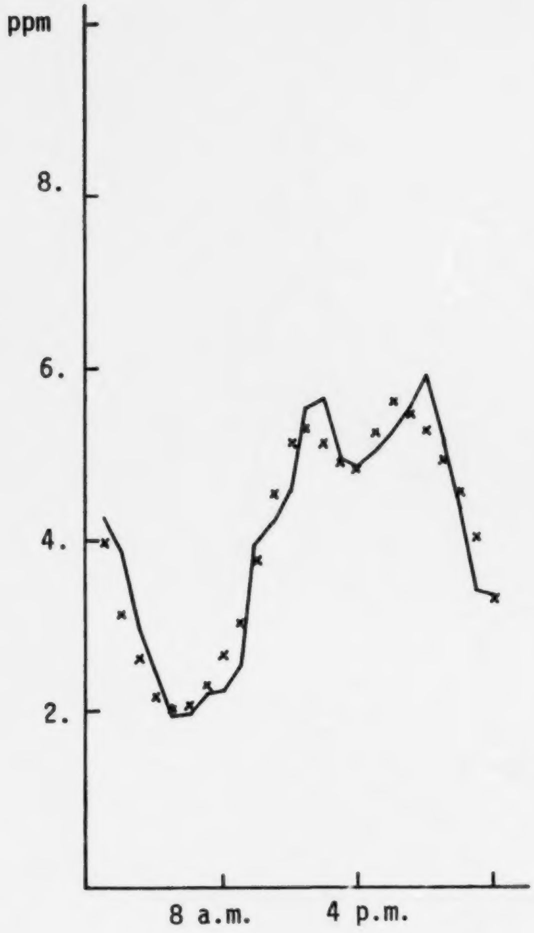
(ii)

Figure 5. CO model summer weekday fit (x predicted - observed).



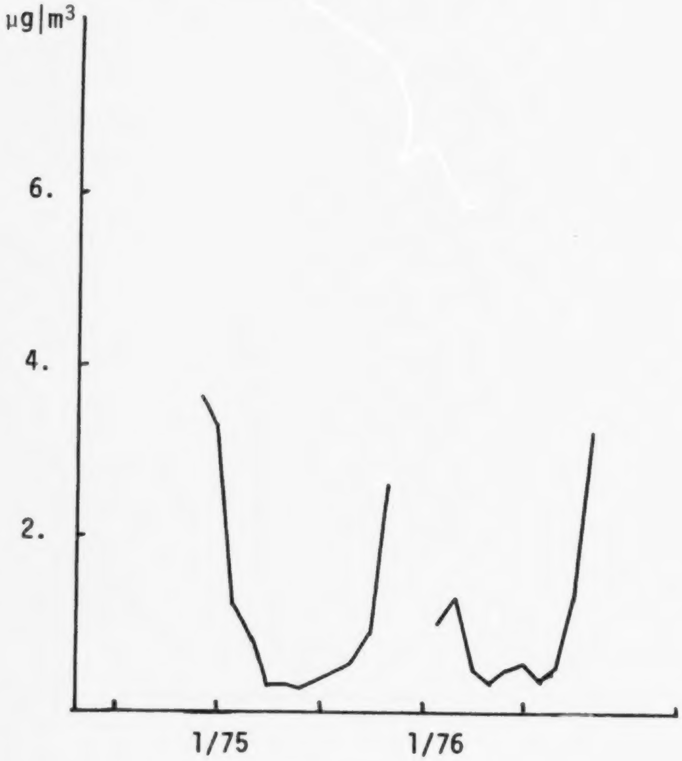
(iii)

Figure 5. CO model winter weekday fit (x predicted - observed).



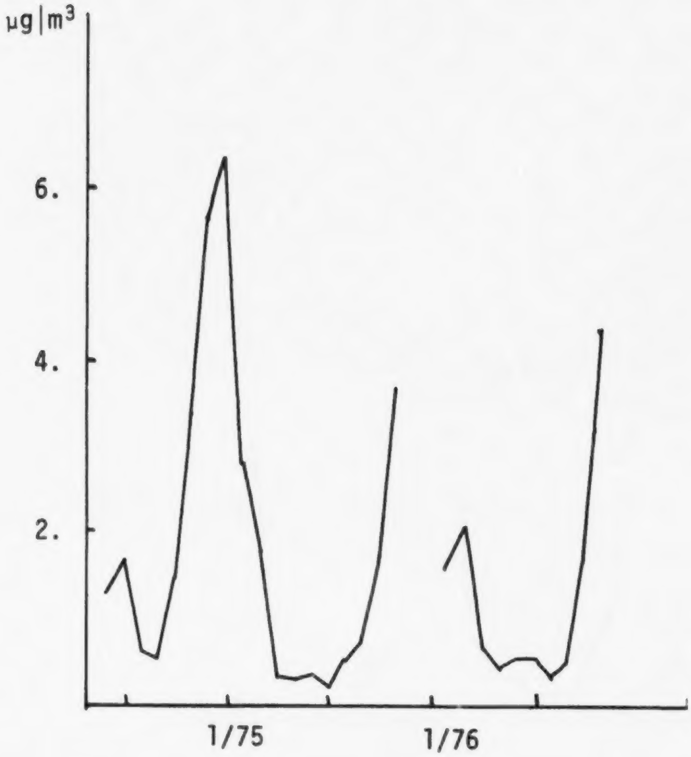
(iv)

Figure 5. CO model summer weekday fit (x predicted - observed).



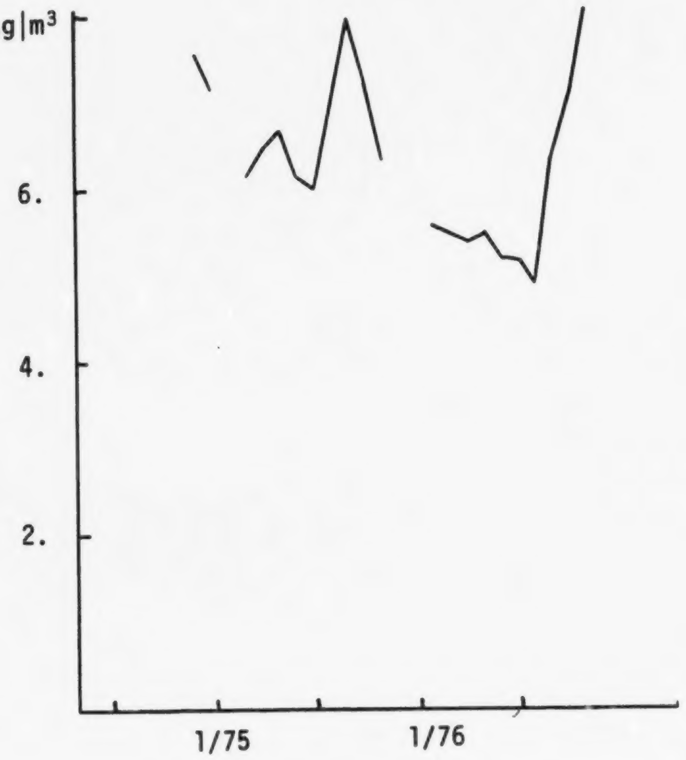
(i) Site A.

Figure 6. Monthly means of 4-hr hi-vol. afternoon readings of Pb for various sites.



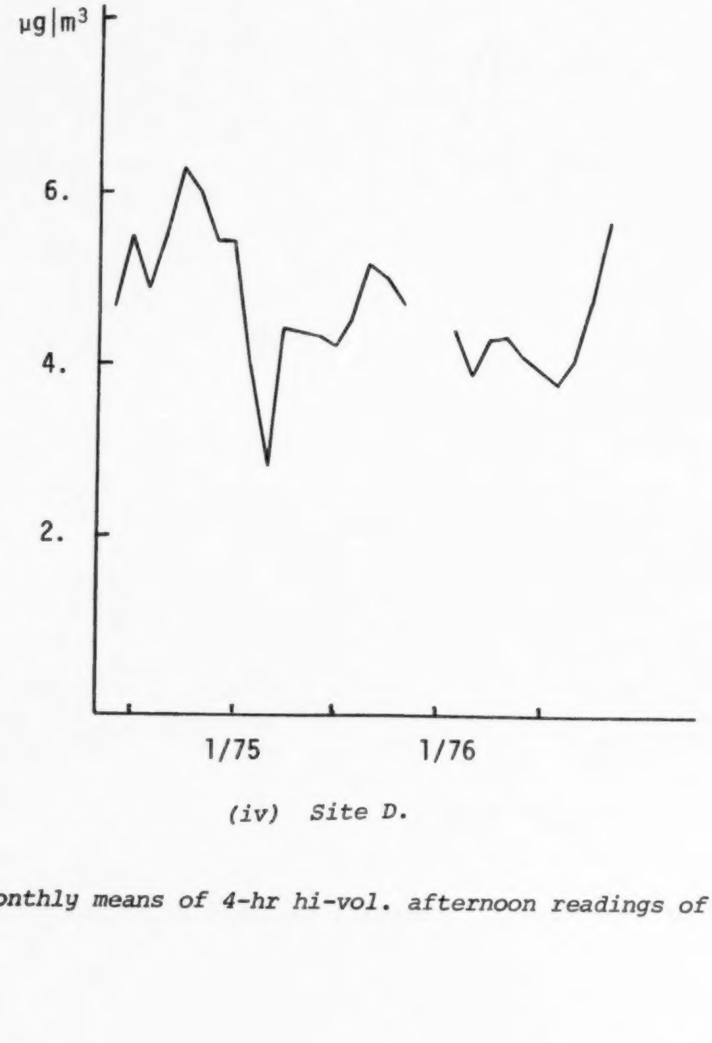
(ii) Site B.

Figure 6. Monthly means of 4-hr hi-vol. afternoon readings of Pb for various sites.



(iii) Site C.

Figure 6. Monthly means of 4-hr hi-vol. afternoon readings of Pb for various sites.



(iv) Site D.

Figure 6. Monthly means of 4-hr hi-vol. afternoon readings of Pb for various sites.

Table IV. SIMPLE T-TESTS TO COMPARE THE SUMMER MEANS OF Pb, 1974-1976 (MAY-OCTOBER)

Site D

Year	mean	s.d.	no. of observations
1974	5.30	1.20	68
1975	4.49	.79	84
1976	4.11	.92	76

Years	t-statistic	sig. Level
1974-1975	4.75	.000
1975-1976	2.79	.006
1974-1976	6.59	.000

Site C

Year	mean	s.d.	no. of observations
1975	6.76	1.40	84
1976	5.80	1.44	76

Years	t-statistic	sig. Level
1975-1976	4.28	.000

$$Pb_{t'} = \alpha' + K' \sum_{t=16}^{19} (TD)_t^{t'} e^{-b(WS_{\perp t}^{t'} - W_o)^2} + a_{t'}$$

t' stands for a particular day,

$(TD)_t^{t'}$ is traffic density at hour t on day t',

$WS_{\perp t}^{t'}$ is perpendicular wind speed at hour t on day t',

a_t' is the error term for day t',

α' is a parameter measuring the background,

K' is a parameter proportional to Pb emissions,

b and W_o are, as before, parameters measuring effect of the wind.

Evaluation of the Trend in Pb Emissions

Model for lead has been used to assess the trend in Pb emissions in a manner similar to that for the CO data. Specifically, we divided the time span of the data into the same five periods as was done in the case of CO. The daily 4 hour (3-7 p.m.) afternoon Pb readings from June 1974 through October 1976, the corresponding hourly $WS_{\perp}$ for the four afternoon hours, together with the (same) average TD figures for these four hours, were then employed to estimate the parameters $\alpha', b, W_o, K_1', \ldots, K_5'$. Here, K_j' measures the Pb emissions for period j, $j=1,\ldots,5$. In an initial fitting α' was found to be insignificant and hence ignored in our final estimation. The parameter estimates of $b, W_o, K_1, \ldots, K_5$ for sites C and D are given in Table V.

We observe that for both sites there was a decrease in Pb emissions. This is probably due to an increased use of unleaded gasoline. Also, the estimated values of the emission constant at site D are lower than those at site C. This seems reasonable because site D is situated farther from the freeway and a part of the lead particles will settle on the ground before reaching D.

Comparison of Weekday and Weekends

As reported earlier (5), we have found that the afternoon Pb readings are substantially higher in the weekends than during the weekdays. The monthly means of both the weekday and weekend afternoon Pb readings for sites C and D are plotted in Figures 6(v) and (vi), respectively. It is clear from these figures that there is a considerable difference; for site C the weekend values are about 60% higher than the weekday values. This increase on the weekend is somewhat puzzling since there is a decrease in traffic density from weekday to weekend [see Figure 4(iv)].

Now, recall from Figure 4(v) that the speed of the traffic decreases drastically during the weekday afternoon rush hours. However, we see from the dotted line in the same figure that such a decrease does not occur on the

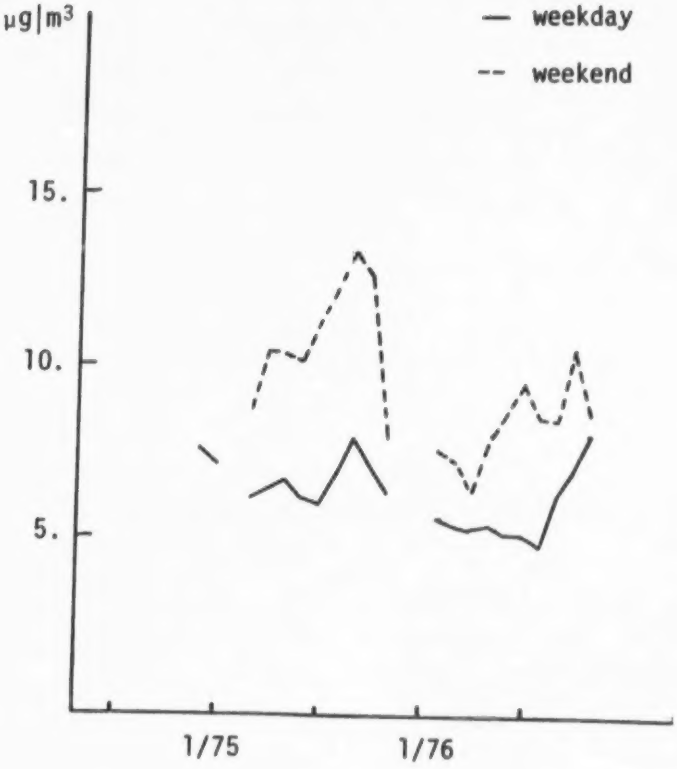
Table V. ASSESSMENT OF Pb TREND

Site C

Period	Parameters	Estimate	Std. Err.
	b	.00013	.00002
	W_o (mph)	2.28	.40
Summer 75	K_3 ($\mu g/m^2$)	.00640	.00023
Winter 75-76	K_4 ($\mu g/m^2$)	.00514	.00025
Summer 76	K_5 ($\mu g/m^2$)	.00514	.00025
	σ_3	1.25	
	σ_4	1.19	
	σ_5	1.44	

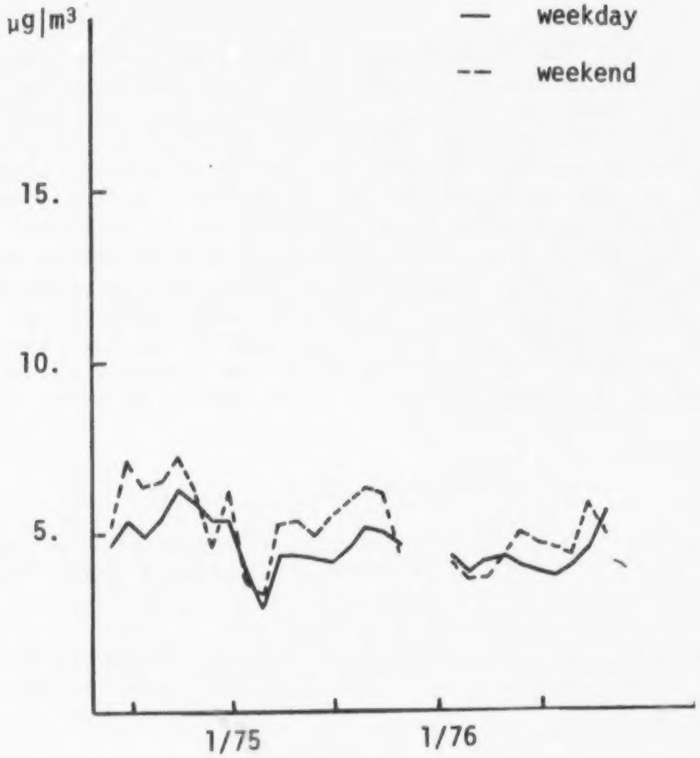
Site D

Period	Parameters	Estimate	Std. Err.
	b	.00020	.00002
	W_o (mph)	2.45	.19
Summer 74	K_1 ($\mu g/m^2$)	.00507	.00013
Winter 74-75	K_2 ($\mu g/m^2$)	.00428	.00021
Summer 75	K_3 ($\mu g/m^2$)	.00454	.00013
Winter 75-76	K_4 ($\mu g/m^2$)	.00416	.00016
Summer 76	K_5 ($\mu g/m^2$)	.00378	.00016
	σ_1	1.00	
	σ_2	1.53	
	σ_3	.50	
	σ_4	.76	
	σ_5	.99	



(v) Site C.

Figure 6. Monthly means of afternoon Pb.



(vi) Site D.

Figure 6. Monthly means of afternoon Pb.

weekend. This would explain the observed weekday to weekend difference if emissions of Pb varied inversely proportionally with the speed of traffic. This theory is partially supported by a comparison of the weekday vs. weekend monthly means of the morning Pb readings shown in Figure 6(vii). Specifically, we observe from Figure 4(v) that, in the morning, the difference between weekday and weekend speed is smaller than that in the afternoon. At the same time Figure 6(vii) indicates that there is no real difference between the weekday and weekend morning Pb readings. In fact, it has been reported in (4) that Pb emissions do tend to vary proportionally with the traffic speed.

Conclusions

We have illustrated for the CO data that a simple model involving the wind speed and traffic density can, to a good approximation, describe the behavior of the pollutant near the freeway. This model has been used in assessing changes in CO and Pb emissions since the introduction of the catalytic converter. We have found a decrease in both CO and Pb emissions, which can probably be attributed to the increased number of catalyst equipped cars on the freeway. We have shown that there is an increase in Pb emissions from the weekday to weekend. This increase is probably due to the increased speed of the traffic on the weekend. In our analysis of the SO_4 data we have found that there is a discrepancy between the 4 hour hi-volume readings and the 4 hour membrane readings. A plausible explanation seems to be that there is an artifact formation on the hi-volume filter causing the discrepancy, but much further research is needed to determine the precise nature of these two sampling techniques.

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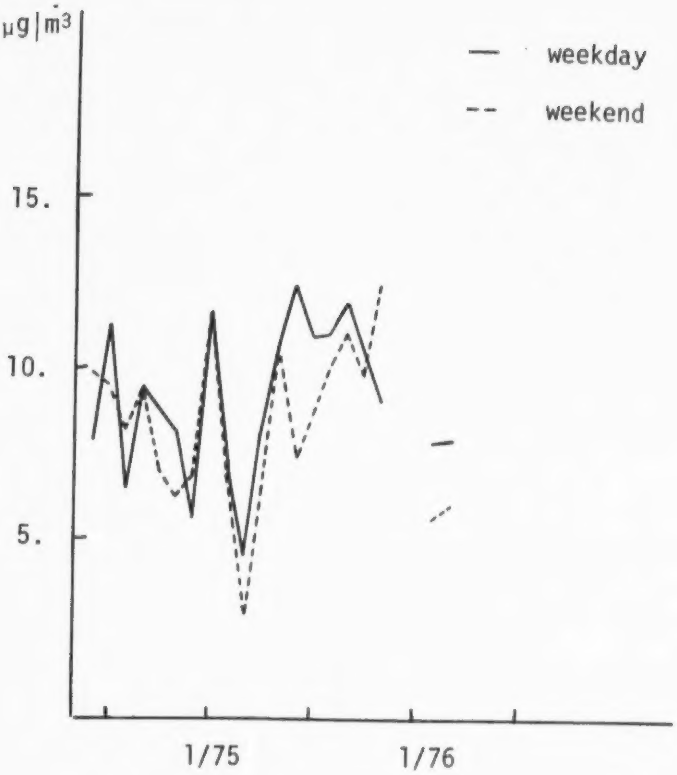

(vii) Site D.

Figure 6. Monthly means of afternoon Pb.

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DISCUSSION

Dr. William Pierson

Ford Motor Company
Dearborn, Michigan

The following observations and estimates (surrogate calculations) were made by Dr. William Pierson of Ford Motor Company at the LACS Symposium utilizing data presented:

In general the sulfur consumption (from the fuel) in automobiles is ~ 50 *mg/mi, including all sizes of* $SO_4^{=}$ *plus* SO_2*. This number may even be higher, especially if diesels are included.*

Pb emissions from non-catalyst cars (Ron Bradow's estimate) are ~ 40 *mg/mi airborne, all sizes.*

Therefore one would expect the ratio of contributions from the freeway at the LACS to be:

$$\left(\frac{\Delta \Sigma S}{Pb}\right) = \sim\frac{50}{40} = \sim 1.2$$

From LACS 24-hour ambient measurements $\Delta SO_2 = \sim 9\ \mu g/m^3\ SO_2 = \sim 4.5\ \mu g/m^3\ S$, $\Delta SO_4^{=}$ *(dichot.)* $= \sim 0.5\ \mu g/m^3\ SO_4^{=} = \sim 0.17\ \mu g/m^3\ S$*, and* $\Delta Pb = \sim 4\ \mu g/m^3$.

Summing the sulfurs and dividing by the Pb:

$$\left(\frac{\Delta SO_4^{=} + \Delta SO_2}{\Delta P}\right) = \frac{.5 + 0.17}{4} = 1.2$$

Examining the ambient moleratio of dichotomous $SO_4^{=}$ *to total sulfur:*

$$\left(\frac{\Delta SO_4^{=}}{\Delta SO_4^{=} + \Delta SO_2}\right) = \frac{0.17}{0.17 + 4.5} = \sim 0.04$$

Assume a 30% catalyst car mix, then the $SO_4^{=}$ *conversion from* *__catalyst__* *cars calculated from ambient measurements would be* $\simeq 0.04/30\% = 0.13$ *or 13%.*

If the ratio of sulfate to Pb contribution

$$\frac{\Delta SO_4^{=}}{\Delta Pb} = \frac{0.5}{4} = 0.125,$$

and if the Pb emission rate is typically = 40 mg/mi, then the calculated emission rate of $SO_4^{=}$ *from all cars would be = 40 x 0.125 =* ~ 5 *mg/mi.*

Again assuming a 30% catalyst car mix: 5/30% = ∿17 mg $SO_4^=$/mi calculated emission rate from catalyst cars based on LACS ambient measurements. Ron Bradow offered 10 mg/mi from actual emission tests.

Conclusions: The preceding estimates indicate that the LACS ambient $SO_4^=$ and Pb measurements are consistent with those predicted from typical emission factors. One could have used CO instead of Pb as the surrogate.

The above estimates are crude and ignored differences in fuel sulfur between leaded and unleaded gasoline. Also I just picked averages off the slides, but it all seems to "hang together."

If the wind-speed dependence of ΔPb_{C-A} is unequal to that of $(\Delta so_4^=)_{C-A}$, then something is seriously wrong.

LOS ANGELES CATALYST STUDY SYMPOSIUM
CONCLUSIONS AND RECOMMENDATIONS

Thomas R. Hauser

Environmental Protection Agency
Research Triangle Park, North Carolina

ACHIEVING OBJECTIVES

At the outset of Los Angeles Catalyst Study (LACS) in June 1974, four prime objectives for the study were established.

The first objective is to determine the impact of catalyst equipped cars on air quality for automobile related pollutants. At the present time, it has been demonstrated that the LACS site is a very adequate site to determine the effect of catalyst emissions on air quality particularly during the summer months between 1500 and 1900 hours. The LACS study has collected a large amount of air quality data with simultaneous meteorology and traffic information, all measured at the same station, accompanied with very extensive quality assurance procedures. Hence this body of data provides a multitude of possible comparisons among various collection methods, analysis methods, and pollutant interrelationships.

The second objective of LACS is to provide an active data base to contrast roadside levels of automobile related pollutants caused by pre- and post-catalyst equipped cars. The study was initiated in June 1974, prior to the introduction of catalysts on cars, and has continued to date. The rigorous quality assurance procedures that have been applied to the LACS attest to the fact that a valid, high quality data base is available from June of 1974 to the present time to make judgments concerning the effect of the addition of catalysts on 1975 and later model year automobiles.

The third objective is to utilize the measured ambient levels of carbon monoxide (CO), lead (Pb), and sulfur dioxide (SO_2) to determine the surrogate (predicted) sulfuric acid ambient levels. Based upon the recent reports that conversion of sulfuric acid (H_2SO_4) to sulfate occurs very rapidly in the ambient air and that the measurement levels of sulfates attributable to the freeway are very low, it appears that surrogate projections of sulfuric acid levels from roadways need to be reevaluated. The methodology for continuous ambient measurement of H_2SO_4 has not been available; however, the measured sulfate contribution (and probably H_2SO_4 levels) from the freeway are substantially less than was expected and do not appear to constitute a serious problem at this time.

The fourth objective is to evaluate and improve field methodology for detection and measurement of air quality changes attributable to catalyst emissions. Based upon the presentations at the LACS Symposium, it is obvious that this objective is being met by evaluating and improving field methodology as the need arises and resources are available. Several intermethod comparisons have been made to solve existing problems and add credibility to the data base.

SPECIFIC CONCLUSIONS

RESULTING FROM CONTINUOUS MEASUREMENTS

- *The LACS site has been shown to be a very favorable location in terms of meteorology and traffic flow for determining freeway contributions, particularly during the summer from 1500-1900 hours.*
- *Traffic flow estimates by the California Department of Transportation coupled with Environmental Protection Agency (EPA) data indicate that there has been little change in the traffic volume on the San Diego Freeway at the study site from 1974 through 1976. The diurnal traffic patterns by day of the week are very consistent. The total number of automobiles passing the catalyst site averages about 188,000 vehicles per day, and by the end of 1976 about 30% of the vehicular miles travelled were attributed to catalyst equipped cars.*
- *The freeway contribution of CO has decreased about 25% since the inception of the study; from 1975 to 1976 the contributions of nitric oxide (NO) and nitrogen dioxide (NO_2) from the freeway have increased more than 50%.*
- *There is an inadequate amount of O_3 at freeway level to convert all of the NO to NO_2. The reaction of NO and ozone (O_3) is rapid enough to result in almost zero concentrations of O_3 at the near downwind site.*
- *The background levels of CO, NO, and NO_2 have remained essentially constant since 1974.*
- *An empirical model relating diurnal behavior of CO to traffic density and perpendicular wind speed has been developed and used to assess the trend of freeway contribution of CO during 74-76.*

RESULTING FROM INTEGRATED MEASUREMENTS

- *The background levels of total suspended particulates (TSP) and Pb have changed very little since the beginning of the study.*
- *The background levels of sulfate have decreased 25% since 1974.*
- *The freeway contributions of TSP and Pb have both decreased ∿25% since 1975.*

- *Previous LACS summary reports indicating freeway contributions of sulfate as high as 5 $\mu g/m^3$ were based on four hour high volume sampler (hi-vol) measurements. These short term measurements by this technique are now thought to be adversely affected by artifact sulfate formation, resulting in erroneously large cross-freeway difference estimates. The concensus of all methods indicates only 0.5 to 1.0 $\mu g/m^3$ freeway contribution of sulfate during periods of favorable meteorology.*

- *The apparent artifact sulfate formation on the hi-vol samples does not appear to be significant in determining 24 hour cross-freeway differences, but seems to contribute a substantial error to four-hour sulfate measurements.*

- *The model for CO has been extended to assess the trend in Pb (4-hour).*

- *During the most favorable meteorology, weekend Pb concentration is ∿60% higher at the downwind site than weekday level. This appears to be related to the slow traffic speed during the weekdays.*

FUTURE LACS MONITORING PROGRAM

The following observations are pertinent concerning the utility of continuing the LACS.

There is a need to continue to evaluate the impact of catalysts on air quality. This will be increasingly important as new catalyst-type vehicles and additional diesel traffic are added to the traffic mix. Our present data base and site are extremely well suited for assessing effects of transportation control strategies on air quality data. It is EMSL's position that only through a long-term monitoring study under appropriate quality control can theoretical and laboratory findings be verified from which Agency regulatory decisions can be based. However, monitoring frequency could possibly be reduced. It is our opinion that at least two more summer seasons of data are necessary to establish a reliable trend using present sampling technology.

The addition of a sensitive, reliable continuous H_2SO_4 analyzer will be made when available to verify our off-roadway estimates of ambient levels. Assuming an acceptable H_2SO_4 analyzer will be available in the near future, data should be gathered to demonstrate the relationship between sulfate measurements and sulfuric acid aerosol.

There is a need for additional in-roadway measurements taken at the fixed site collected in the median as well as mobile sampling around the LACS area. Knowledge of spatial variability together with our temporal variability studies will provide us the means from which theoretical population exposure estimates can be verified. In addition, in-vehicular concentrations should be determined as needed.

There is still a definite need to quantify the amount of sulfate artifact formation on filters used to monitor sulfate at the LACS site.

It is intended that time series models will be developed to concurrently employ data from all sites to estimate spatial and temporal variability across the freeway. This will include fixed in-roadway and mobile monitoring data. Time series models for other pollutants including one for NO-NO_2-O_3 will be required to judge what effect future oxides of nitrogen (NO_x) control strategies may have on ambient concentrations off the roadway.

The present data base contains information to assist EPA in examining a variety of other equally important issues associated with transportation control. Some examples are: (a) establishment of the proposed Pb standard; (b) input to the formulation of an oxidant control strategy; (c) examination of the cross-freeway relationships of the NO_x and O_3; and (d) verification of the relationships between auto emission measurements and actual ambient levels at the roadside. It should be noted that an additional two summer seasons of data will greatly augment this data base.

At present, EPA is concerned with environmental insult due to toxic substances, some of which are emitted from mobile sources, e.g., PAN, benzene, etc. Maintaining surveillance of air quality in proximity of major roadways could serve to identify and determine trends of air quality due to pollutants from mobile sources for the purpose of determining the need for and effect of control measures. Such a monitoring program could also be used to measure the presence of toxic substances identified by the Fuel and Fuel Additive Registration Program.